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NUCLEAR DIVISION

MARTIN

BALTIMORE 3, MARYLAND

ANPP CORROSION PROGRAM

Final Summary Report

MND-E-2727

February 1962

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FOREWORD

This report was prepared by the Nuclear Division of the Martin Company for submission to the Nuclear Power Field Office, Engineer Research and Development Laboratories, U. S. Army Corps of Engineers.

The report was prepared under Contract DA-44-009-ENG-3581 and summarizes the results of the ANPP Corrosion Program.

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SUMMARY

This report summarizes the results of four years of corrosion testing performed by the Nuclear Division of the Martin Company for the U. S. Army Corps of Engineers, under the ANPP Corrosion Program. The objectives of the program were to investigate the suitability of various materials for heat exchanger fabrication in nuclear power plants and to investigate the effects of various water treatments on the performance of these materials. Static autoclave and dynamic loop tests were performed.

The results of these tests have shown conclusively that Inconel is superior to all other materials tested in simulated nuclear service. A wide range of environments from high purity water to water containing high chloride concentrations was used. The criteria of comparison were: resistance to general corrosion, pitting corrosion, crevice corrosion and susceptibility to stress corrosion cracking.

AISI Type 304 austenitic stainless steel, AISI Type 430 ferritic stainless steel, Inconel, Monel and nickel were tested in tilting autoclaves. Test exposures varied considerably, as did environmental composition. The Type 304 stainless steel cracked severely in 120-hour tests. The Type 430 stainless steel pitted badly in 120-hour tests. Inconel suffered very slight incipient attack after 2000 hours' exposure to a severe environment. Both Monel and nickel pitted somewhat after 2000 hours' exposure to a severe environment.

Miniature heat exchangers tubed with AISI Type 304 stainless steel, Croloy 16-1, bimetal with low-carbon steel facing the secondary, Inconel, Monel and nickel were tested for varying times in a wide range of environments. Two of the three Type 304 stainless steel heat exchangers cracked and failed within a short time--one after only 42 hours' exposure. Two of the three Croloy 16-1 vessels failed, and all three suffered rather severe pitting. None of the three bimetal miniature vessels with low carbon steel on the secondary side failed, but all showed varying degrees of pitting and gross loss of surface metal. The four Inconel vessels suffered nothing more than superficial attack, even after long exposures to environments containing high concentrations of dissolved chloride. The two Monel vessels and the two nickel vessels were pitted to varying degrees.

Model configuration heat exchangers tubed with AISI Type 304 stainless steel, Croloy 16-1, bimetal with low carbon steel facing the secondary, and Inconel were tested under conditions comparable to the miniature vessels. The model vessels were tested in sets consisting of one steam generator and one superheater in series. The superheater of the Type 304 stainless steel set failed after about 2000 hours.

The secondary environment in the steam generator contained about 50 ppm chloride. The two sets of bimetal model heat exchangers suffered varying degrees of corrosion in proportion to their conditions of exposure. The set with Croloy 16-1 tubes, particularly the superheater, pitted severely. The Inconel test vessels (two sets) were attacked only superficially. No Monel or nickel model heat exchangers were tested in this phase of the program.

I. INTRODUCTION

The pressurized water reactor plant occupies a prominent position in the Army Nuclear Power Program, with several such plants already in operation and a number of others under construction. In these plants, the primary water coolant transfers heat from the reactor core to the secondary system via the steam generator. Thus, the steam generator tubing is exposed to the high purity, though radioactive, primary stream, as well as to the lower purity secondary water. The reliability and long life essential for ANPP plants dictates the use of high performance materials for steam generator fabrication. The ANPP Corrosion Program was implemented to investigate experimentally this area of plant design and development.

The objectives of the ANPP Corrosion Program are to determine the applicability of various metals for use in heat exchangers and to investigate the type and extent of corrosion in specified environments. Specifically, this includes:

(1) The determination of the effects of secondary water conditions on heat exchanger life, using various exchanger materials. The most severe single water condition is limited to 1000 ppm chloride with air-saturated water and air as a cover gas.

(2) The examination of the techniques used in test heat exchanger fabrication.

(3) The recommendation of materials and service conditions for operating heat exchangers.

The general procedure for meeting these objectives evolved, during the course of the program, into the following:

(1) A broad range of water conditions for a particular material is investigated in rocking autoclave tests. A more definitive range of water conditions is then selected on the basis of autoclave test results, e.g., satisfactory and unsatisfactory.

(2) Miniature heat exchangers (MHX-X), of the general configuration shown in Fig. 17, are tested to verify the autoclave results. On this basis, further narrowing of the range of water conditions is obtained.

(3) Specific water conditions, based on the results of Steps (1) and (2) are then selected for use in the testing of model heat exchangers (Mod SG-X or SH-X) of the general configuration shown in Fig. 38.

The design of the smaller (miniature) test heat exchangers underwent modification during the course of the program. Initially, the miniature heat exchangers had a sealed secondary system in which there was a certain amount of dynamic cycling in that the secondary water was continuously steamed and condensed by an integral cooling coil (see Fig. 16). However, there was no replenishment of the constituents of the secondary environment. Miniature Heat Exchangers 1 through 9 were tested under these conditions. Both the design and mode of test of the miniature test vessels were subsequently modified (see Fig. 17). The mode of the test was made fully dynamic, and Miniature Heat Exchangers 10 through 19 (excepting MIN 12 and 17 which were not used) were tested in this manner

The design of the model heat exchangers underwent only minor changes, which will be noted later in the report. The primary flow system for the model heat exchangers underwent only very slight modification during the period of tests. The secondary flow system was modified to a considerable degree. Initially, one feed pump and one make-up tank served both sets of test vessels, as did the condensate return line. This, naturally, resulted in some intermixing of environments with attendant difficulties in maintaining the required conditions in the two steam generators. Two sets of model vessels could be tested simultaneously. The difficulties of maintaining the specified conditions were compounded by the unequal steaming rates. The normal carryover of each system was concentrated more rapidly in the vessel with the higher steaming rate. The model heat exchangers designated SX-1, SX-2, SX-5 and SX-6 were tested under these circumstances. Subsequently, the secondary flow systems were modified so that each was separated completely from the other. There was no opportunity for cross contamination, as in previous tests. The model heat exchangers designated SX-4 and SX-7 were tested under these circumstances.

Generally, the secondary environments of the test vessels were very severe, so that differences between the metals tested would be apparent within a reasonable test time.

This report is intended to summarize the overall program and to review the conclusions and recommendations which have been drawn from the test results. Topical reports should be consulted for more details concerning any particular phase of the work. Autoclave tests are described in Refs. 1, 2, 5 and 8. Loop tests are described in Refs. 3, 4, 6 and 10. Methods and procedures employed in the program, as well as a detailed description of the facilities, are given in Ref. 7.

II. AUTOCLAVE DESCRIPTION AND TECHNIQUES

As mentioned previously, investigation of a material begins with autoclave tests, where either U-bend or beam specimens are exposed to both the vapor and liquid phases in environments ranging from high quality water to water containing considerable quantities of dissolved constituents such as chloride.

A. PHYSICAL DESCRIPTION

Three AISI Type 304 stainless steel tilting autoclaves were used in the ANPP Corrosion Program. The internal dimensions are 2-1/16 inches by 32 inches in depth. The wall thickness is 1-1/8 inches. All three of the autoclaves were hydrostatically tested cold at 18,000 psi. The electrical heating jackets are wired in two sections, top and bottom, and are individually controllable. Each autoclave is provided with a rupture disc for safety. The rocker mechanisms are driven by air motors. An electrical timer actuates the rocker mechanism through a solenoid valve in the air line. Rocking of the autoclave occurs for one two-minute period every two hours. They move through an arc of 85 degrees, starting at 35 degrees from the vertical, about 18 times per minute. Figure 1 is a photograph of the autoclaves.

B. AUTOCLAVE SETUP

Prior to all tests, the autoclaves are washed with an acetone saturated cloth, then rinsed with hot distilled water until the silver nitrate test for chloride in the rinse water is negative. Finally, the autoclaves are rinsed with demineralized water of one million ohm-centimeter resistivity.

Several methods for setting up the autoclaves are used, depending upon the desired composition of the atmosphere. The simplest method is to place the desired liquid environment into the autoclave, insert the test device and seal the autoclave with its entrapped air. The volume of liquid used is chosen so that, at operating temperature, the autoclave will be half filled with liquid. An appropriate allowance is made for the displacement of the test device. The environmental water, in all cases, had been previously adjusted to the proper concentration of dissolved constituents and adjusted to the desired pH.

If low environmental oxygen concentrations are required, the procedure is modified. The test device and environmental water are placed in the autoclave, which is then sealed. The autoclave is evacuated, by a high pressure line, to a predetermined pressure level, maintained at that pressure for about half an hour, and then sealed.

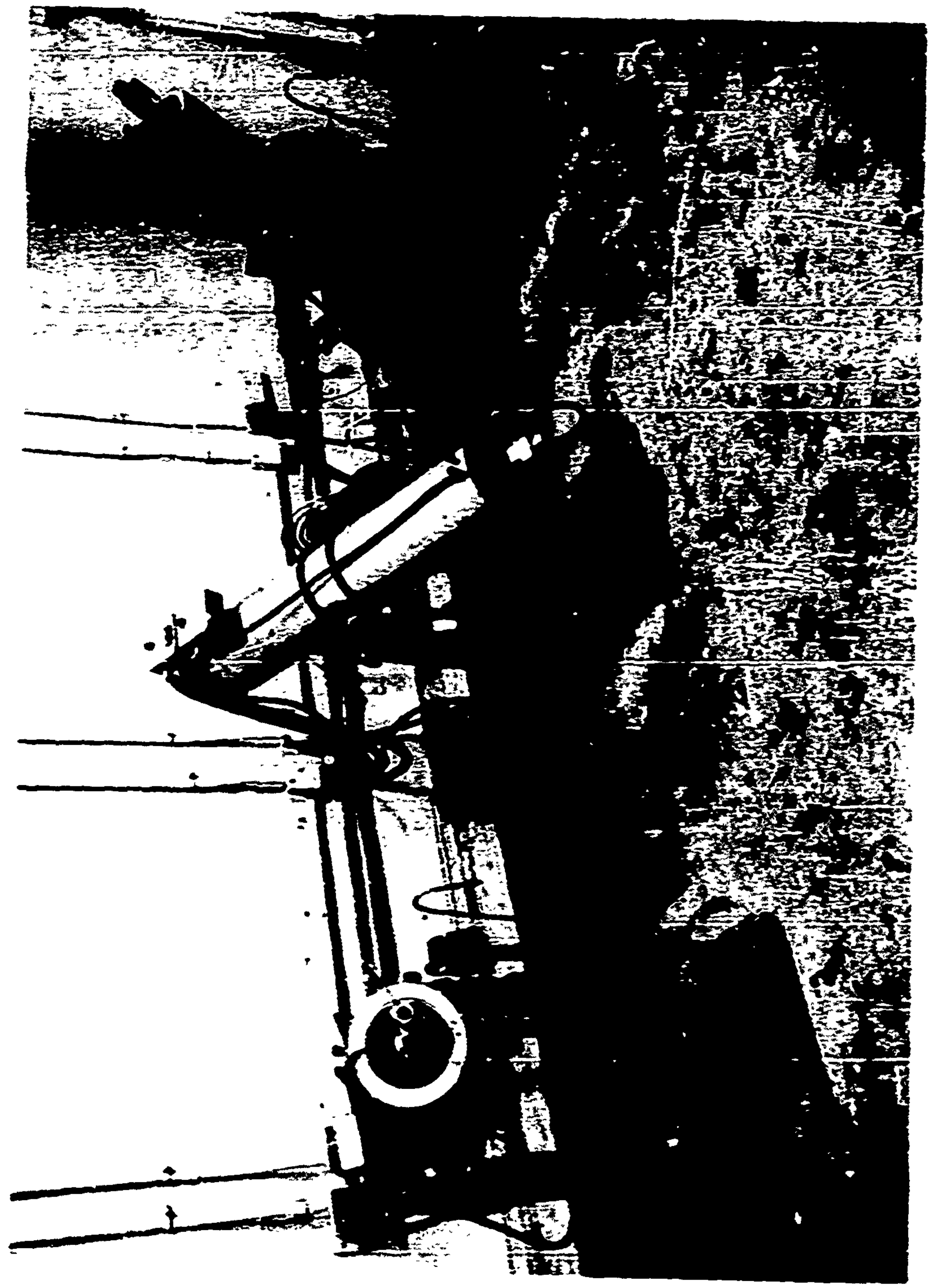

Fig. 1. Rocking Autoclaves

If it is desired that a single gas (for example, oxygen) be present in the environmental vapor space, the following procedure is used. The autoclave is evacuated to 50 microns. The desired amount of freshly boiled or oxygen-saturated liquid environment is drawn into the autoclave. Finally, the autoclave is backfilled to the desired oxygen pressure and sealed.

The concentration of dissolved oxygen in the water will have been established with stationary autoclaves where specific setup procedures were followed. A sampling tube, which extends to the bottom of the autoclave, permits sampling the autoclave water during operation. Sampling is done in an evacuated stainless steel McLean tube. Water samples and, in some cases, vapor samples are taken before and after each test.

III. AUTOCLAVE TESTS AND RESULTS

The materials tested in autoclaves were AISI Type 304 stainless steel, AISI Type 430 stainless steel, Inconel, Monel and nickel.* The type specimens used for the first three metals were U-bend. Beam specimens were used in the last series of tests. The purpose of the autoclave tests was to provide a rough screening of the materials which were to be tested and to aid in specifying test parameters for subsequent static and dynamic tests.

A. TESTS WITH AISI TYPE 304 STAINLESS STEEL

1. Sample Preparation

The specimens were fabricated from a sheet of 1/8-inch thick Type 304 stainless steel, which was obtained in the mill annealed, as-rolled condition for this purpose. The sheet was sheared into 1-inch by 6-inch specimens. The specimens were annealed at 1150° C for 15 minutes in a hydrogen atmosphere. The short exposure prevented excessive grain growth. The samples were formed in U-bends around a 1-inch diameter rod which was pressed into an appropriately sized die. The open legs were left about 1-3/8 inches apart. They were closed to an approximately 1-inch separation immediately before testing by drawing the legs together with a Type 304 stainless steel bolt. All the specimens were inspected visually and with radiography after forming, and none showed any evidence of cracks.

2. Sample Holders

Three sample holders were fabricated from Type 304 stainless steel rod, Type 304 stainless steel bolts and Teflon. The Teflon was cut to fit tightly against the inside diameter of the autoclave and indented to hold the horseshoe sample tightly in place. One side of the Teflon was removable, so that the U-bend specimen could be mounted easily. The Teflon holders were attached to the ends of a single Type 304 stainless steel rod cut to the inside length of the autoclave. The specimens contacted only the Teflon during the test and were, therefore, insulated from the autoclave. Figure 2 is a photograph of the sample holder with specimens attached.

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*Material compositions are summarized in Appendix A.

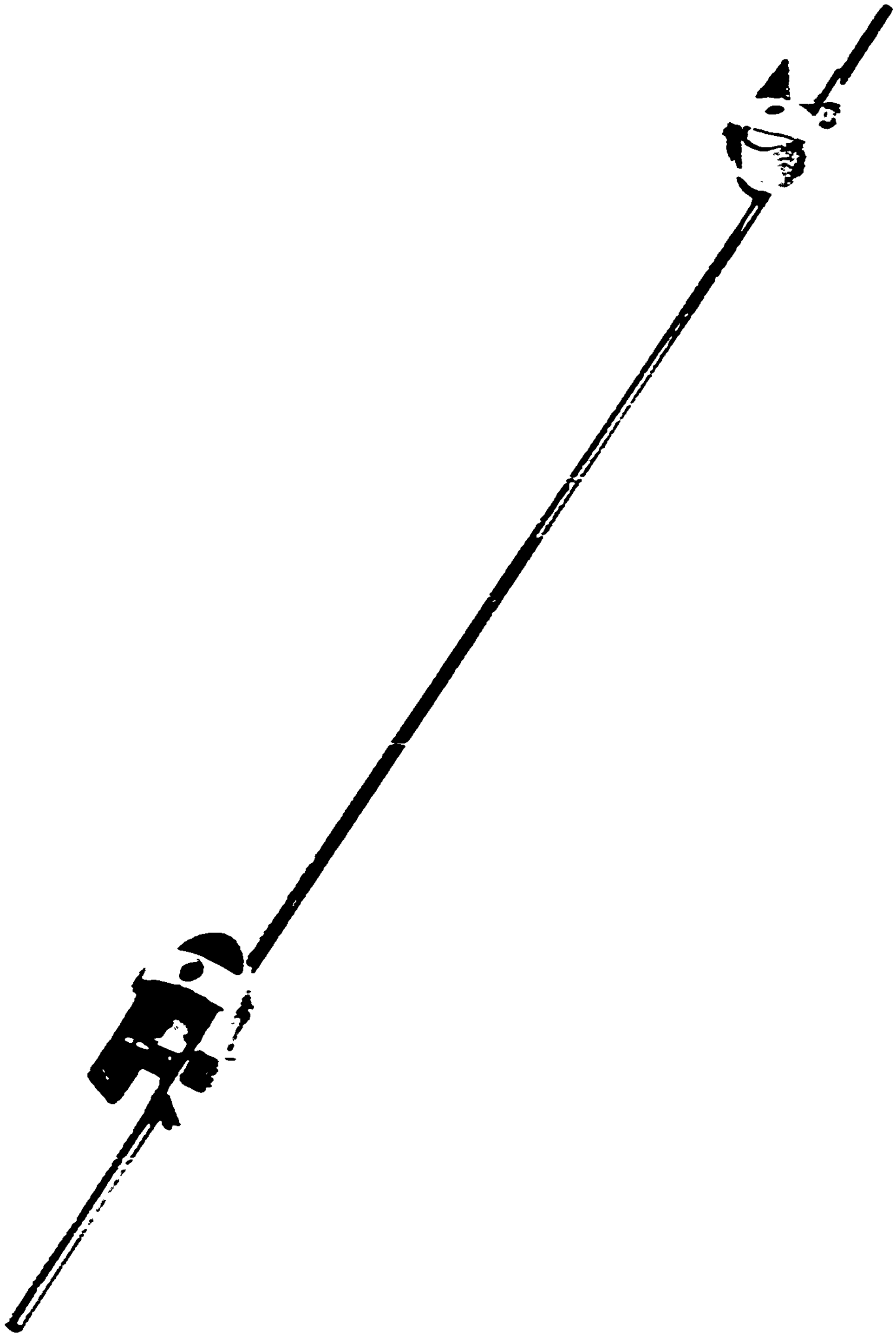

Fig. 2. Sample Holder with Specimens Attached

3. Environmental Controls

The controlled conditions and constituents were: chloride concentration, phosphate concentration, pH and the oxygen content of the water and vapor phase. Other variables included the use of tap water, distilled water and distilled deionized water for make-up. The pH was adjusted to three levels: 8.5, 10.5 or 11.5. The concentration of the phosphate ranged from near zero to over 400 ppm, and chloride concentration varied from near zero to slightly over 1300 ppm. The concentration of oxygen in both the water and vapor phases varied from near zero to perhaps 100% vapor, in which case the amount of oxygen dissolved in the water amounted to perhaps 15 or 20 ppm. The concentration of oxygen in water at operating temperatures varied according to Henry's Law, $K = \frac{Pa}{Na}$, where K for oxygen at 400° F = 6.56×10^5 and Pa, the partial pressure, is calculated from the equation $PV = nRT$, which shows that about 0.7 ppm oxygen is dissolved in the water per % of oxygen in the atmosphere at 400° F and 250 psia. Therefore, with 5% oxygen in the atmosphere, 3.5 ppm will be dissolved in the water. The relationship expressed by Henry's Law is true only when the components are intimately mixed, which is not the case in an autoclave used in these tests. Therefore, the results shown represent maximum possible oxygen concentrations; the actual concentrations are somewhat less. The autoclave atmosphere was tested for oxygen after each test in an effort to confirm the designated starting concentration.

Temperature was controlled at 195 ± 10° C. This seemingly large variation was due to intentional temperature difference between the steam and water phases. The maximum variation occurred immediately following each rocking cycle when the water was exposed to high vapor space temperature.

4. Stress Level Calculations

The AISI Type 304 stainless steel specimens used for these tests were bent to 1/2 inch inside radius. The stress level during test was accepted as the tensile stress in the outer fibers of the specimens, associated with the amount of plastic elongation at that point. It was calculated that the outer fibers were elongated 11% during bending. Immediately prior to the corrosion test, the legs of the specimens were drawn together to re-establish the stresses that were developed during bending. Thus, the outer fibers were stressed to the yield point of the material, which had been elongated 11%. The high incidence of cracking indicates that the required stress threshold was surpassed.

5. Results

Typical results of some Type 304 stainless steel samples are shown in Table 1. Of the 36 specimens tested (18 in each phase) 13 cracked. All but two of these were in the vapor phase. Figure 3 is a typical photomicrograph of one of the specimens that cracked.

B. TESTS WITH AISI TYPE 430 STAINLESS STEEL

1. Sample Preparation and Treatment

A slab of 1/8-inch thick Type 430 stainless steel sheet was obtained in the mill-annealed, as-rolled condition to be used for sample material. The sheet was sheared into 1-inch x 6-inch specimens. The specimens were then annealed. U-bends were cold formed from the flat pieces by bending them around a 1-inch diameter rod in a lubricated die. The open legs were left 1-3/8 inch apart. The legs were compressed to approximately 1-inch separation, immediately before testing, with a Teflon insulated bolt. Visual inspection and radiography did not reveal any cracks in the samples after forming.

The samples were cleaned in 20% HNO_3-2% HF at 120° F to remove the thin oxide film, exposed to 5% oxalic acid, then electropolished by the glycolic acid method. All samples were passivated in 25% HNO_3 at 120° F, rinsed, dried and weighed. Immediately prior to exposure in the autoclave, the samples were activated by a one-minute dip in 50% HCl and rinsed. Post test cleaning consisted of a treatment in 10% NaOH-5% $KMnO_4$ at 200° F to complete oxidation of the oxide film, followed by treatment in 5% oxalic acid. This cleaning was repeated as required and, in the few cases where this process was inadequate, the pieces were cathodically treated in 10% H_2SO_4 to remove the last traces of oxide, again exposed to 5% oxalic acid, rinsed, dried and weighed again.

2. Sample Holders

The sample holders described in Section III-A-2 were used.

3. Environmental Controls

The variables of greatest interest were: pH; the concentration of phosphates, chlorides and oxygen; and temperature, with its dependent pressure. Other variables were: tap, distilled or deionized make-up water. Various combinations of concentrations, ranging to 1100 ppm chloride, 335 ppm phosphate, 100% oxygen in the vapor space, and pH

TABLE 1

Test Results of AISI Type 304 Stainless Steel U-Bend Specimens

Specimen Exposure*	Test Time (h)	Make Up Water	Initial pH	Average Phosphate (ppm)	Average Chloride (ppm)	Maximum Oxygen Concentration in Vapor Space (Vol. %)	Weight Loss $(mg/dm^2/mo)$	Penetration Rate (mpy)	Condition of Surface: Before Test	Condition of Surface: After Test
L	120	tap	11,5	15	10	5,0	10,07	0,06	chemically polished	no cracking
L	120	tap	10,4	140	32	0,0	5,33	0,03	chemically polished	no cracking
V	120	tap	11,5	13	10,7	10,8	14,07	0,085	chemically polished	no cracking
V	120	tap	11,5	54	944	10,7	21,83	0,132	chemically polished	pitted and cracked
V	168	deionized	8,5	72	830	10,0	3,56	0,02	chemically polished	moderate cracking
V	120	deionized	10,4	10	975	22,0	139,24	0,84	chemically polished	badly cracked
V	120	tap	11,5	15	1130	16,6	48,19	0,29	chemically polished	moderate cracking
V	120	distilled	11,2	none	1220	10,4	18,76	0,113	chemically polished	moderate cracking
L	120	distilled	11,2	none	1220	22,0	51,27	0,31	preoxidized	cracked
V	120	deionized	8,5	290	130	100,0	14,4	0,087	chemically polished	no cracking
V	648	distilled	10,4	none	800	6,6	18,27	0,111	chemically polished	slight cracking
L	648	deionized	10,4	none	125	22,0	51,20	0,30	chemically polished	cracked

*L = Liquid, V = Vapor

Fig. 3. Photomicrograph of Type 304 Stainless Steel Specimen Autoclaved 120 Hours in Vapor Phase. Water Environment Contained 980 ppm Cl, 10 ppm PO_4 at pH 10.4.

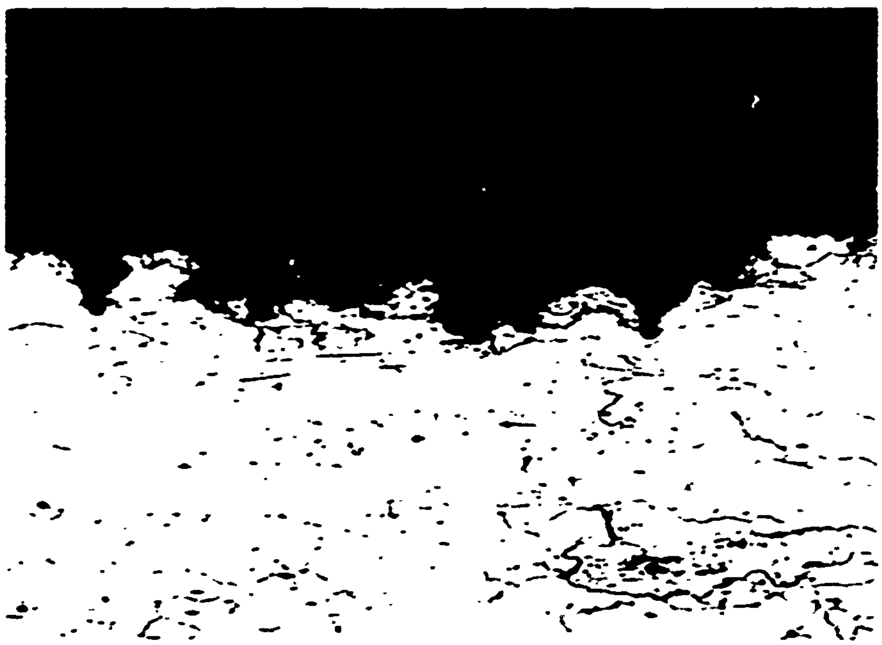

Fig. 4. Type 430 Stainless Steel Exposed to Vapor Phase of Water Containing 990 ppm Cl. Pits Are About 4 Mils Deep
Magn 250x

ranging from 8.5 to 11.5 were employed. Temperature was controlled as in the previous tests. Exposure time in one series was extended from the usual 120 hours to 1176 hours to determine if stress corrosion cracking would occur with the longer exposure.

4. Stress Level Calculations

The AISI Type 430 stainless steel U-bend specimens were formed around a 1-inch diameter rod. The outer fibers of the specimen were calculated to be elongated 11%. The stress level during test was accepted as the tensile stress in the outer fibers of the specimen associated with the amount of plastic elongation at that point. Immediately prior to the corrosion test, the legs of the specimens were drawn together to re-establish the stresses that were developed during bending. Thus, the outer fibers were stressed to the yield point of the material that had been elongated 11%.

5. Results

None of the 52 specimens tested cracked, despite the severe conditions used. Exposure time in one series was extended from the usual 120 hours to 1176 hours; still, none cracked. Half of the vapor phase specimens pitted, which was not an unexpected occurrence, since the ferritic stainless steels are known to be susceptible to pitting in chloride environments. The pits ranged to a maximum of four mils in depth. Three of the 26 specimens immersed in water were pitted. In the 120-hour tests, phosphate decreased the tendency of specimens to pit in both the vapor and liquid phases. However, when the test time was extended sufficiently, specimens in both phases pitted. Two cleaning methods, electropolishing and chemical cleaning, were investigated superficially and were found to be indistinguishable by any of the test results. Figure 4 shows a typical pitted surface.

C. AUTOCLAVE TESTING OF INCONEL

1. Sample Preparation and Treatment

A sheet of annealed wrought Inconel 1/8 inch thick was sheared into coupons, each 1 inch x 6 inches. Weld specimens, located at the phase interface, were tested, along with vapor phase and water phase specimens. The weld specimens were made by the inert gas shielded tungsten arc process with Inco "A" filler wire. The bead was laid along the length of one side of five coupons. The weld specimens were not bent into U-bend configuration. The remaining 15 specimens were cold formed by bending each around a 1-inch mandrel, leaving the legs 1-3/8 inches apart. The legs were compressed to 1-inch separation by a Teflon-insulated bolt immediately before testing. Visual

inspection and radiography did not show any cracks in the samples after forming. The specimens were attached to the stainless steel holders used previously. In each experiment, one U-bend specimen was in vapor, one was immersed in the environmental water and the weld specimen was exposed vertically at the vapor-water interface. All specimens were degreased in perchlorethylene, rinsed in acetone, dried in vacuum and weighed. After the test, the specimens were descaled in a 10% NaOH-5% $KMnO_4$ solution at 200° F to loosen the oxide. This was followed by treatment in a 5% oxalic acid solution.

2. Environmental Controls

The environmental test conditions for the 500-hour autoclave tests at 500° F and 680 psi are shown in Table 2.

TABLE 2

Environmental Conditions for Inconel Autoclave Tests

Test	Chloride (ppm)	Oxygen: Water* (cm^3/kg)	Oxygen: Vapor** (%)	Adjusted pH to 10 with
1	50	15	21	Sodium phosphate
2	1000	15	21	Sodium phosphate
3	50	15	21	Sodium hydroxide
4	50	0.1	0.5	Sodium phosphate
5	1000	15	21	No pH adjustment

*Defined as oxygen dissolved in water at operating temperature and pressure.

**Concentration of oxygen in vapor space at ambient temperature.

3. Stress Level Calculations

The stress in the outer fibers of the U-bend specimen was determined by an indirect method. The stress level was established as being the tensile stress associated with the amount of plastic elongation found to occur in the outer fibers of the specimen. The elongation of the outer fiber was determined by the following procedure:

(1) Uniformly spaced lines were scribed (0.040 inch apart) on an unbent specimen in the area to be subjected to maximum bending.

(2) The line spacings were measured to the nearest 0.00025 inch.

(3) A U-bend specimen was formed from the scribed piece with the scribed lines on the outer surface.

(4) The spacing between lines was remeasured to the nearest 0.00025 inch.

(5) The percent elongation was calculated from the change in line spacings.

(6) The average value for three or four spaces was determined.

The stress level associated with this amount of elongation was determined by conducting tensile tests on the same lot of material. The extensometer used had a range which extended to the predetermined amount of plastic elongation. The tensile stress was determined from the stress-strain curve. A line was projected parallel to the slope of the modulus of elasticity from the elongation axis to the curve. The applied stress value was read on the stress axis. This value was considered to be the stress in the outer fibers of the U-bend specimens in the bolted position.

The data determined for the Inconel U-bend specimens used in this program is as follows:

Material Properties (room temperature)

Yield strength	39,400 psi
Ultimate tensile strength	93,500 psi
Elongation in two-inch gage section	47%
Modulus of elasticity	31.4×10^6 psi

Specimen Stress Determination

Elongation of outer fiber, average of two specimens	10.5%
Associated stress level, 10.5% elongation	83,500 psi

4. Results

Table 3 is a compilation of the data from this series of tests.

TABLE 3

Inconel Autoclave Tests

500° F and 680 psi for 500 hours

Test Number	Test Condition	Specimen Test Phase	Corrosion Rate ($mg/dm^2/mo$)	Corrosion Rate (mpy)
1	50 ppm Cl air cover gas pH 10 with PO_4	vapor	52.8	0.30
		liquid	42.0	0.24
		interface*	15.0	0.08
2	1000 ppm Cl air cover gas pH 10 with PO_4	vapor	93.8	0.53
		liquid	66.5	0.37
		interface*	49.4	0.28
3	50 ppm Cl air cover gas pH 10 with PO_4	vapor	43.2	0.24
		liquid	60.8	0.34
		interface*	31.6	0.17
4	50 ppm Cl low O_2 pH 10 with PO_4	vapor	93.1	0.52
		liquid	87.5	0.49
		interface*	50.2	0.28
5	1000 ppm Cl air cover gas No pH adjustment Initial pH 5.0	vapor	56.4	0.32
		liquid	46.9	0.26
		interface*	159.9	0.90

*Weld specimen

None of the 15 Inconel specimens cracked or pitted, despite the severe environmental conditions. A dull brown adherent film of corrosion products was formed on all the specimens, but there was not enough loose scale to make an X-ray diffraction analysis. No cracks were located by the dye penetrant test, and metallographic examination showed no change in the Inconel.

A comparison of the data shows that when phosphate is present, the water phase specimen has a lower corrosion rate than the vapor phase specimen. The converse is true when sodium hydroxide is used to adjust the pH.

It is obvious that Inconel possesses good inherent corrosion resistance to chloride media up to 260° C. The highest corrosion rate measured was less than one mil per year.

D. AUTOCLAVE TESTING OF MONEL, NICKEL AND INCONEL

An investigation of possible ways to improve the autoclave test program led to the selection of a statistically designed experiment. One of the many outstanding advantages of a designed experiment is the inherent ability to determine main effects and interaction effects of the independent variables with assurance. It is nearly impossible to determine the latter with any other type of experiment. The factorial design lends itself readily to mathematical evaluation as well as graphic presentation of the results. The basic purpose of the designed experiment was to determine the relative resistance of Monel and nickel to general corrosion under various environmental conditions. In addition, a few selected tests with Inconel were planned for comparison.

1. Sample Preparation and Treatment

The material supplier selected Monel and nickel tubing 2-1/2 inches in diameter with 5/16-inch wall thickness from individual heats. Some of this tubing was drawn to 3/4-inch OD, with a 0.65-inch thick wall. This tubing was set aside for use in the fabrication of test heat exchangers. The remainder of the tubing was split, flattened and rolled to sheet 3 inches wide, 1/8 inch thick and 72 inches long.

The as-received Monel sheet was rolled to 0.080 inch and fully annealed in a hydrogen atmosphere at 790° C for one hour; nickel was annealed in a hydrogen atmosphere at 730° C for one hour. The annealed strips were deoxidized, then further reduced to 0.040-inch thickness, producing 50% cold work. Test coupons and tensile specimens were sheared and numbered. The coupons were rinsed in acetone, pickled in dilute hydrochloride acid, rinsed in hot distilled water and dried in a heated air blast to prevent water staining. Half of each type of coupon was fully annealed, as above, and the remainder of both types of coupon was stress-relieved at 232° C for one hour.

The Inconel specimens were prepared in the same manner, i.e., 0.080-inch Inconel was fully annealed at 980° C for 15 minutes in a hydrogen atmosphere. The thickness was reduced to 0.040 inch, which produced 50% cold work. Tensile specimens and test coupons were sheared, and half of each type was annealed at 980° C for 15 minutes in a hydrogen atmosphere, and the other half was stress relieved at 430° C in air for one hour.

All of the test coupons--Monel, Inconel and nickel--were three inches long, 1/2 inch wide and 0.040 inch thick. Beam specimens were substituted for U-bend specimens in these tests for several reasons, including the large number of specimens in each test in a limited autoclave volume and better control of stress level. After testing, these specimens were examined for pitting, cracking and other evidence of local attack, but these factors entered into the statistical analysis only to the extent that they affected the weight loss due to corrosion. Therefore, acceptable descaling techniques were of prime importance.

Many methods were evaluated in an effort to find an acceptable descaling process. These methods included: (1) cathodic treatment in 5% sulfuric acid inhibited with 0.8 gram per liter ethylquinolinium iodide, followed by a dip in 10% nitric acid or 10% ammonium hydroxide; (2) a treatment in boiling 25% sulfamic acid for one hour; (3) an alkaline permanganate (10% NaOH-5% $KMnO_4$) and 10% oxalic acid process; and (4) cathodic treatment in 10% caustic solution, followed by a dip in 10% nitric acid.

The descaling method concluded to be the best for Monel and nickel coupons was the sulfamic acid bath. This treatment consisted of exposing the corroded coupons to boiling 25% sulfamic acid for one hour. After removal from the descaling bath, the coupons were rinsed in water, rinsed in acetone, then dried with an electrically heated blower. The blank correction is 2.3×10^{-5} gm/cm^2. Although this blank correction was in some cases close to the oxide weight, it was considerably lower than the correction of any other method evaluated.

The descaling method concluded to be the best for Inconel was the alkaline permanganate-oxalic acid procedure. This treatment consisted of exposing the corroded coupons to an alkaline permanganate solution to loosen the oxide, followed by exposure to 10% oxalic acid. The blank correction is 4.3×10^{-5} gm/cm^2.

2. Sample Holders

The holders for the specimens were fabricated of Inconel with Teflon and diamonite insulators. Each holder supports 12 specimens, 6 stressed and 6 unstressed. The beam specimens were supported at both ends. Stress was applied by adjusting a fine-thread screw, which loaded the beam at the midpoint. Two holders were used in each autoclave, one in the liquid phase and one in the vapor phase. Figure 5 is a photograph of the sample holder with coupons mounted.

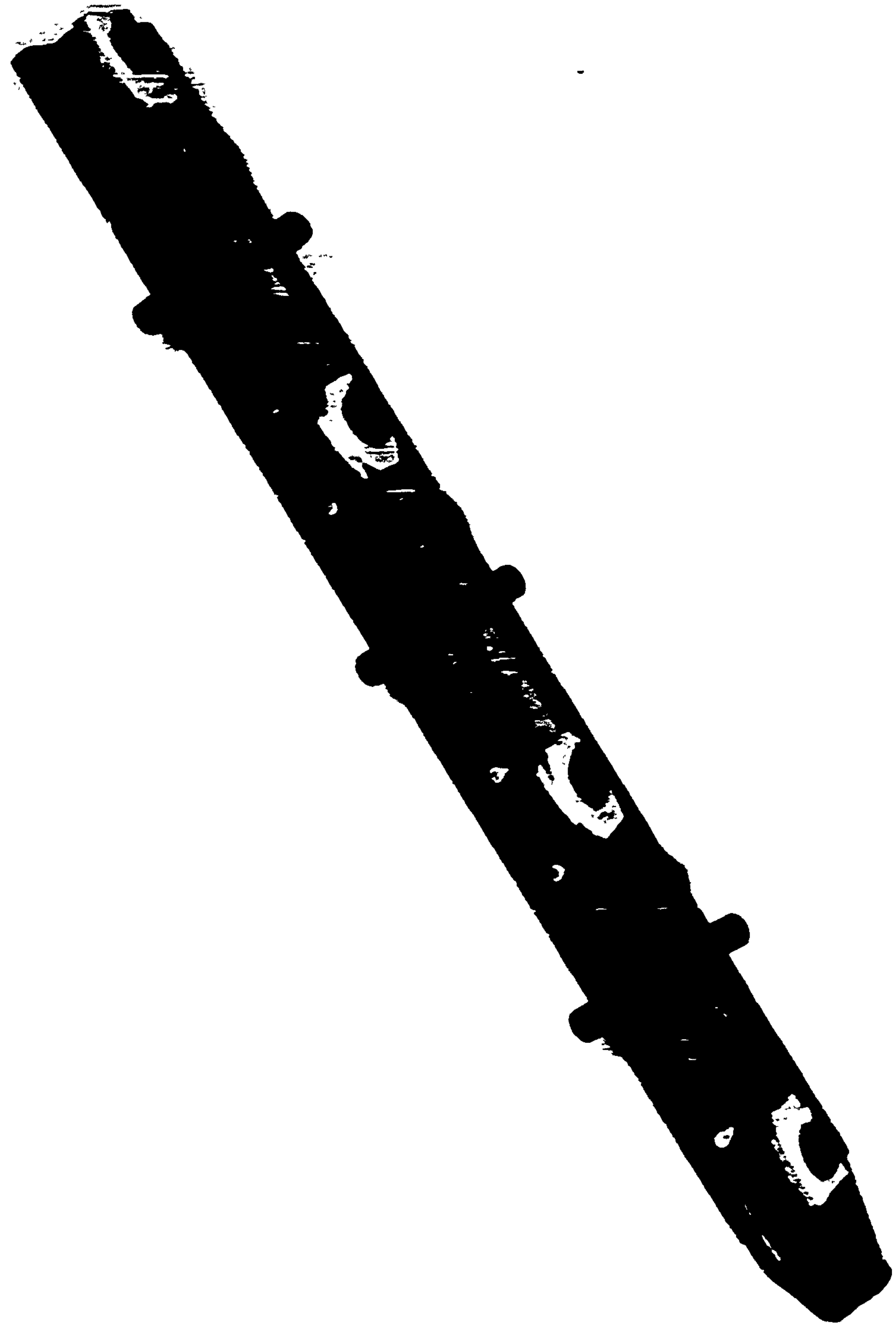

Fig. 5. One-Half Section of Autoclave Rack for Beam Specimens. The Sections Are Joined at Threaded Ends with a Threaded Rod

3. Environment Controls and Experimental Design

There were eight experimental factors. Each factor had two levels, except chloride and time, which had three. These were:

Factors	Levels
Material	Monel and nickel
Chloride	10 ppm, 100 ppm and 1000 ppm
Alkalizing agent (pH 10)	Na_3PO_4 and NaOH
Oxygen*	Low (~1 ppm) and high (~15 ppm)
Heat treatment	Annealed and stress-relieved
Stress level	Unstressed and stressed to 90% yield
Phase	Vapor and liquid
Time	50, 200 and 2000 hours

*The initial concentration of oxygen dissolved in the water at operating temperatures.

Stock solutions of all the water treatment chemicals for use throughout the program were prepared prior to initial tests. These included N/10 $Na_3PO_4 \cdot 12\ H_2O$, N/10 NaOH and a large supply of NaCl solution from which aliquot portions were withdrawn and properly diluted in volumetric glassware to produce the 10 ppm, 100 ppm and 1000 ppm Cl solutions. The Na_3PO_4 solution used to adjust the pH was back titrated with enough Na_2HPO_4 to assure that there was no free alkali in the solution. Deionized water was used in the preparation of all solutions.

Three autoclaves, randomly assigned, were used for the experiment. Chloride, oxygen and pH adjustment were the conditions imposed within each autoclave. In the block diagram shown in Fig. 6, these factors and the materials are the column factors. There were three row factors: heat treatment, stress level and phase. The two classes of each row were run simultaneously within an autoclave and three specimens were exposed to each set of conditions. Thus, 24 coupons were exposed in each autoclave run. This procedure ruled out fractionalizing the replicates among the row factors. Also because of information losses, particularly concerning possible interactions, a fractional factorial was not considered. The test program indicated by Fig. 6 was used for the 200-hour tests. Since each column in Fig. 6 represents one test run, this series consists of 24 runs.

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			Monel												Nickel											
			Cl_1				Cl_2				Cl_3				Cl_1				Cl_2				Cl_3			
			pH_1		pH_2		pH_1		pH_2		pH_1		pH_2		pH_1		pH_2		pH_1		pH_2		pH_1		pH_2	
			O_1	O_2	O_1	O_2	O_1	O_2	O_1	O_2	O_1	O_2	O_1	O_2	O_1	O_2	O_1	O_2	O_1	O_2	O_1	O_2	O_1	O_2	O_1	O_2
HT_1	S	V																								
		L																								
	U	V																								
		L																								
HT_2	S	V																								
		L																								
	U	V																								
		L																								
Total																										

Fig. 6. Autoclave Test Program--200 Hours

Corrosion tests were also run for 50 and 2000 hours. The test programs for each exposure time are indicated in Figs. 7 and 8. Table 4 defines the symbols used in Figs. 6, 7 and 8.

TABLE 4

Definition of Symbols

Symbol	Definition
Cl_1	10 ppm chloride
Cl_2	100 ppm chloride
Cl_3	1000 ppm chloride
O_1	1 ppm oxygen
O_2	15 ppm oxygen
pH_1	NaOH
pH_2	Na_3PO_4
HT_1	Annealed
HT_2	Stressed relieved
S	Stressed
U	Unstressed
V	Vapor phase
L	Liquid phase

All tests were run at 232° C to prevent stress relief of the coupons during test. For precisely the same reason, all coupons that were not annealed were stress relieved at 232° C prior to being stressed for test.

4. Stress Level Calculations

A number of supplemental tests were performed on autoclave specimens and on the specimen materials to provide data to establish specimen parameters for the autoclave program. These included tensile tests on Monel, nickel and Inconel specimens and determination of strain-deflection curves for autoclave specimens.

			Monel				Nickel			
			Cl_1		Cl_3		Cl_1		Cl_3	
			O_1	O_2	O_1	O_2	O_1	O_2	O_1	O_2
HT_1	S	V								
		L								
	U	V								
		L								
HT_2	S	V								
		L								
	U	V								
		L								
Total										

Fig. 7. Autoclave Test Program--50 Hours

			Monel		Nickel		Inconel	
			Cl_1 O_1	Cl_3 O_2	Cl_1 O_1	Cl_3 O_2	Cl_1 O_1	Cl_3 O_2
HT_1	S	V						
		L						
	U	V						
		L						
HT_2	S	V						
		L						
	U	V						
		L						
Total								

Fig. 8. Autoclave Test Program--2000 Hours

Six Monel and six nickel tensile specimens were fabricated from the same material used for the autoclave coupons. The tensile specimens were machined after the final roll to 0.040-inch thickness; test specimens were cut from the same material. One-half of the Monel and nickel tensile specimens were fully annealed at 790° and 730° C, respectively, for one hour. The other half of the tensile specimens was stress relieved at 232° C for one hour. The results of the tensile tests on these specimens and Inconel specimens similarly prepared are shown in Table 5. The values given are averages of three determinations. Deviations from the averages were less than 2% in all cases.

TABLE 5

Physical Properties of Autoclave Coupon Materials
(average of three values)

	Yield Strength (psi)	90% of Yield Strength (psi)	Proportional Limit (psi)	Ultimate Tensile Strength (psi)	Modulus of Elasticity $\times 10^{-6}$	Percent Elongation (2 in.)
Monel (stress relieved)	123,700	111,000	79,000	126,470	28	28
Monel (annealed)	33,015	27,000	28,000	78,630	24.5	24.5
Nickel (stress relieved)	109,060	98,200	82,000	121,665	32.0	32.0
Nickel (annealed)	19,115	17,200	10,250	74,080	29.1	29.1
Inconel (stress relieved)	166,600	149,940	131,600	169,600	29.6	29.6
Inconel (annealed)	32,860	29,574	23,600	93,200	26.7	26.7

Figure 9 shows a typical stress-strain curve for stress relieved Monel. A stress level of 90% of the yield strength (0.2% offset) was chosen arbitrarily for stressing the autoclave beam specimens. The total strain associated with 90% of yield stress was determined directly from the curve. For example, in Fig. 9, this total strain is 0.00433 in./in.

Strain-deflection curves were determined for several typical beam-type specimens. An SR-4 strain gage was attached to the center of the coupons, which were then deflected in 5-mil increments. Strain versus deflection was plotted. Since the strain-deflection relationship is independent of material properties, the same curve was used for all coupons. The deflection required to produce the strain corresponding to 90% yield stress was determined from the strain-deflection curve. The deflections employed are listed in Table 6.

TABLE 6

Coupon Deflections

Material	Condition	Deflection (mils)
Monel	Fully annealed	46.0
Monel	Stress relieved	126.0
Nickel	Fully annealed	18.5
Nickel	Stress relieved	86.0
Inconel	Fully annealed	42.0
Inconel	Stress relieved	155.0

5. Results*

The results of those autoclave tests confirmed that, under the varied and severe test conditions used, nickel, Monel and Inconel are not susceptible to stress corrosion cracking, and they are very resistant to corrosion. An incipient surface attack was noted on some of the Monel and nickel specimens that were tested for 50 and 200 hours, but none of the specimens cracked or pitted. No cracking of

*For a detailed statistical analysis see Ref. 8.

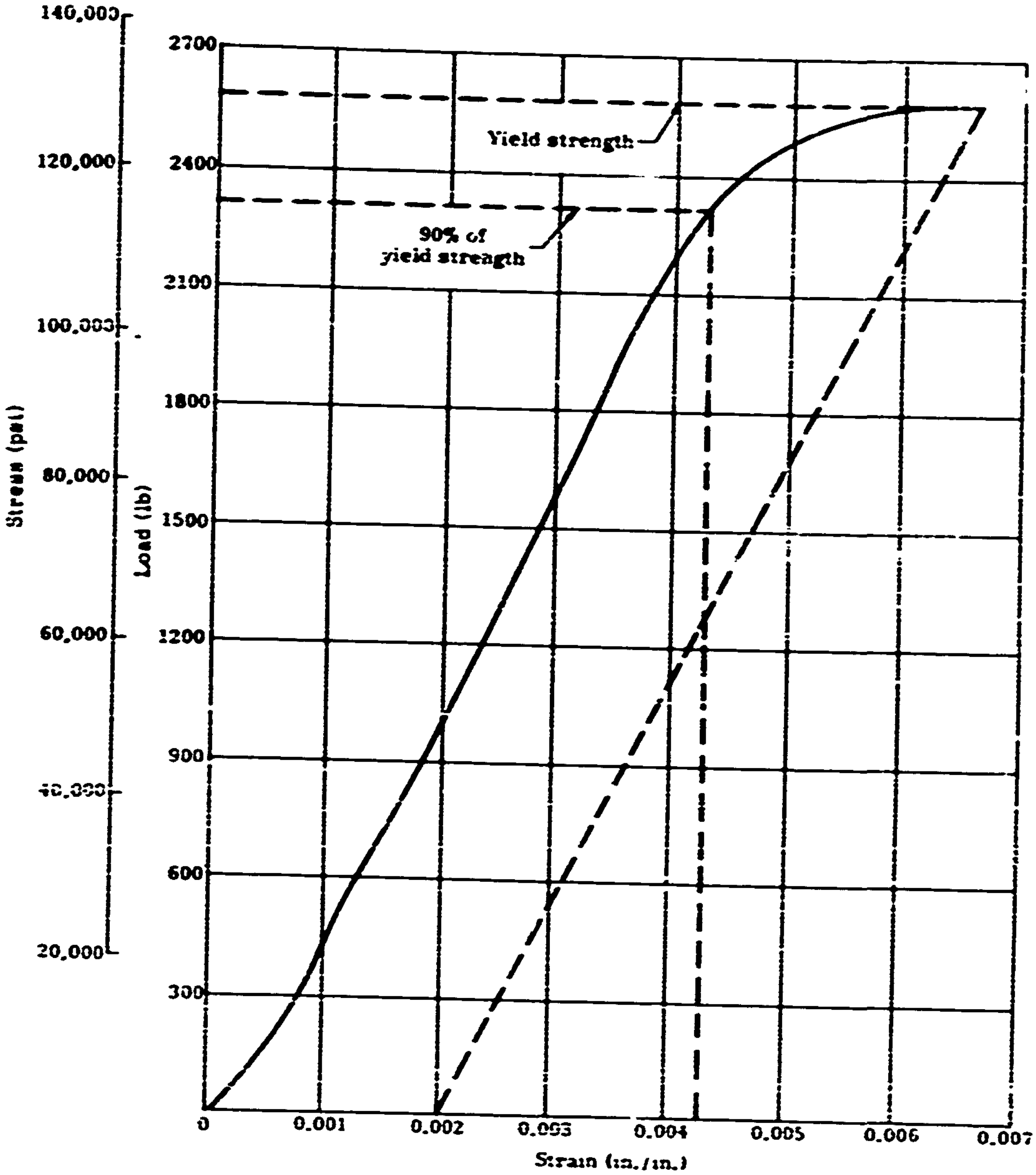


Fig. 9. Stress-Strain Curve for Stress Relieved Monel

any coupons was observed in the 2000-hour autoclave test, but varying degrees of attack and some pitting did occur.

The coupons from the 2000-hour test presented a more meaningful appearance than those from the previous shorter tests, because there is a definite criterion for direct visual comparison. The Monel vapor phase specimens exposed to high chloride, high oxygen pitted mildly as shown in Fig. 10. All 12 of the vapor phase coupons, but none of the liquid phase coupons, suffered attack. No significant difference in attack was noted between stressed and unstressed coupons or between annealed and stress-relieved coupons. The attack occurred on both the tension and compression surfaces of the coupons. The affected areas were relatively large, but shallow, with the average depth about 1 mil. Frequently, a centrally located pit with a diameter-to-depth ratio of about two was surrounded by an area of shallow attack, which was perhaps 50 to 60 mils in diameter. In some instances, more than one pit occurred in the area of attack. The maximum penetration measured was 1.5 mils. A photomicrograph of a typical pit is shown in Fig. 11. No pitting or attacked areas occurred on the Monel coupon in either the vapor or liquid phase in the low chloride, low oxygen test.

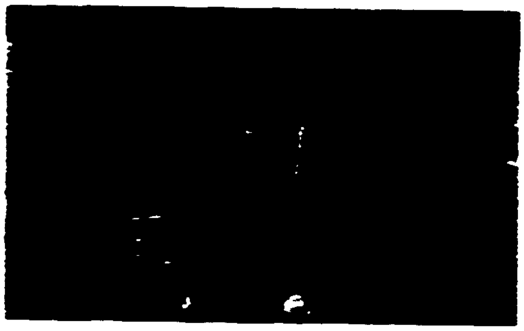
The nickel coupons exposed to vapor in the 2000-hour, high chloride, high oxygen test were attacked mildly also. Both the tension and the compression surfaces were affected, but the tension surface was worse. There was a slightly greater attack on the stress-relieved coupons than on the annealed coupons. The liquid phase coupons were attacked also, but very slightly. The pits in most cases were hardly more than incipient attack. Four of the 12 specimens were pitted; the maximum depth found was 0.5 mil. Coupons in the low chloride, low oxygen test were also pitted. Five of the 12 vapor phase coupons were attacked. One coupon has only three pits, but the other four had perhaps 200 pits per square inch. The physical condition of the specimen (heat treatment and stress) appeared to have no effect on pitting. Five of the 12 water phase specimens were also pitted. They, too, were liberally covered with pits. The appearance of pits on both vapor and water phase coupons contrasted sharply with the previously noted shallow attack on Monel coupons. The ratio of diameter to depth was about two; however, there was no surrounding area of attack. The maximum depth found was 1.5 mils. A photomicrograph is shown in Fig. 12.

Half of the Inconel vapor phase coupons in the high chloride, high oxygen test showed very shallow attack, as in Fig. 13. An isolated pit found on one of the coupons was four mils deep, but generally the pits were no deeper than about one mil. The attack occurred on both the tension and compression surfaces of the coupons and appeared to be about evenly divided, so far as heat treatment and stress were concerned. A photomicrograph of a typical pit is shown in Fig. 14.

Vapor phase
1000 ppm cl
15 ppm O_2

ph 10 (Na_3PO_4)
2000-hr exposure

Fig. 10. Portion of Monel Coupon Showing Incidence of Pitting (6.5 Mag)



Vapor phase:
1000 ppm Cl
15 ppm O_2

pH 10 (Na_3PO_4)
2000-hr exposure

Fig. 11 Photomicrograph of Monel Specimen Showing 0.0014-Inch Deep Pitted Area (250x Mag)

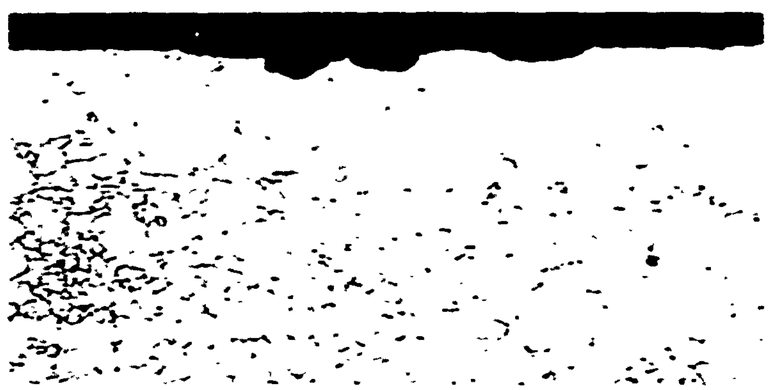
Vapor phase:
1000 ppm Cl
15 ppm O_2

pH 10 (Na_3PO_4)
2000-hr exposure

Fig. 12. Photomicrograph of Nickel Specimen Showing 0.00035-Inch Deep Pit (750x Mag)

Vapor phase:
1000 ppm Cl pH 10 (Na_3PO_4)
15 ppm O_2 2000-hr exposure

Fig. 13. Portion of Inconel Coupon (6.5x Mag)



Vapor phase:
1000 ppm Cl pH 10 (Na_3PO_4)
15 ppm O_2 2000-hr exposure

Fig. 14. Photomicrograph of Inconel Specimen Showing 0.0016-Inch Deep Pit (125x Mag)

No attack was noted on the coupons in vapor or liquid phases of the low chloride, low oxygen test.

The results of these autoclave tests confirm that nickel, Monel and Inconel are not susceptible to stress corrosion cracking under the varied test conditions used, and their resistance to general corrosion is excellent, even for severe environmental exposure. The test results indicate that the corrosion rate of Inconel is much lower than that of Monel and nickel for comparable conditions. An incipient surface dulling was noted on some of the Monel and nickel specimens that were tested for 50 and 200 hours, but none of the specimens cracked or pitted. No cracking of any coupons was observed in the 2000-hour autoclave tests, but varying degrees of attack and/or pitting did occur on all three materials.

Corrosion rates are listed in Table 7. These are time average rates from the results of the 2000-hour tests. The values are also averaged over the stressed, unstressed, annealed and stress-relieved coupons. The superiority of Inconel is clearly evident.

TABLE 7

Comparison of Corrosion Rates for Inconel, Monel and Nickel--2000-Hour Test

		Nickel (mdd)	Monel (mdd)	Inconel (mdd)
10 ppm chloride	Vapor	0.38	0.50	0.02
1 ppm oxygen	Liquid	0.36	0.51	0.04
1000 ppm chloride	Vapor	0.28	0.46	0.02
15 ppm oxygen	Liquid	0.26	0.37	0.03

It is indicated by the data shown in Table 7, that in those systems where chloride is present in amounts within the range of these tests, it is advantageous to have considerably more than 1 ppm oxygen, presumably to maintain the protective oxide film. No attempt was made to determine if there is an optimum oxygen concentration. It cannot be supposed that 15 ppm oxygen necessarily approaches the optimum concentration required to maintain the natural protective oxide film. A similar protective mechanism has been suggested for other systems when other materials were involved (Ref. 12).

The conclusions resulting from the analysis of variance which was performed on the test data are presented below:

(1) The stress level was not a significant factor in the corrosion processes tested (all tests). However, it must be remembered that the stresses were primarily uniaxial and not nearly as complex as those stresses which occur in a fabricated component, such as a steam generator.

(2) In general, the NaOH was a more favorable means of pH control than the Na_3PO_4 except at the lowest chloride level of 10 ppm (2000-hour experiment). This is particularly interesting because nickel and nickel alloys are accepted as fully resistant to caustic; therefore, caustic treatment may be used with these materials.

(3) Inconel has the highest corrosion resistance of the metals tested (2000-hour experiment).

(4) In general, Monel is superior to nickel at 50 hours, while after 200 and 2000 hours, nickel is more corrosion resistant than Monel. The major exceptions occurred in the 200-hour experiment, where the interactions with oxygen, phase, heat treatment and chloride are considerable (all tests).

(5) In general, corrosive attack on all metals is more severe in the vapor than in the liquid phase (all tests).

(6) The annealing heat treatment was generally slightly more advantageous than stress relieving; this is particularly evident in the 2000-hour Inconel tests. However, there are a number of exceptions to this conclusion (all tests). In actual practice, this is generally of academic interest because it is impossible to anneal a large complex structure.

(7) The lower oxygen concentration was more favorable. A few exceptions to this occurred in the 200-hour experiment.

(8) There was considerable interaction between the chloride and oxygen effects on corrosion. In many cases, an increase in chloride concentration (from lowest to highest) at lower oxygen decreased the amount of corrosion, while an increase in chloride concentration at higher oxygen increased the amount of corrosion. However, there were many exceptions to this statement. In the 200-hour experiment, there was much evidence of minimum weight loss occurring between 10 and 100 ppm chloride concentrations for the higher oxygen concentration.

(9) The combined chloride, oxygen variable produced less corrosion when at its lower level (10 ppm chloride, 1 ppm oxygen) in the 50- and 200-hour exposure times, but after 2000 hours, this influence was reversed and the higher level (1000 ppm chloride, 15 ppm oxygen) resulted in less corrosion.

(10) The rate at which corrosion occurred over the first 200 hours was, for the most part, considerably greater for the combined chloride-oxygen variable at its upper level. After 200 hours, the rate decreased and approached zero. For the combined oxygen-chloride variable at its lower level, the corrosion rate was essentially constant.

IV. CORROSION LOOP FACILITY

After preliminary investigations by means of autoclave testing, the materials of interest were used to fabricate scaled-down heat exchangers of two configurations (referred to as miniature and model test vessels) and tested in a high temperature, high pressure loop under simulated plant operating conditions. The loop facility can accommodate four miniature vessels and two sets of model vessels simultaneously. A set of model vessels consists of a steam generator (SG-N) and a superheater (SH-N) in series. The test vessels, when installed, are an integral part of the loop. However, the use of flanged and tube fitting connections make installation and replacement relatively simple.

The facility consists of a primary system which furnishes heat for all of the test vessels. Each set of model vessels has an individual secondary test system, while a third secondary test system serves the four miniature vessels. The facility control system requires manual startup operations, but thereafter all test parameters are maintained by automatic controls. Safety interlocks provide for automatic shutdown in the event of a malfunction. The primary loop design parameters were 3000 psia and 700° F. However, all tests were conducted with the primary at 1200 psia and 450° F. Primary water was circulated through the miniatures at an average rate of 8 gpm and through the model superheater and model steam generator at about 17.5 gpm. This primary water flow through the hairpin tubes of the heat exchanger delivers heat to the secondary at a flux of about 25,000 Btu/ft^2/hr.

The secondary water for the model vessels was preheated to 246° F before being pumped into the steam generator, which operated at 382° F, saturation temperature at the operating pressure of 200 psi. The steaming rate was specified as 60 lb/hr. In the superheater, the steam temperature was raised to 407° F.

Temperatures and pressures for the miniature test vessels were the same as those of the model steam generator. The prescribed steaming rate was 8 lb/hr. All of the secondary conditions given above are nominal; minor deviations due to tube scaling, loop characteristics, etc., occurred during the test program (see Refs. 3, 4, 6 and 10).

In both model and miniature secondary systems, steam was condensed in cooling coils and returned to a make-up tank. Provisions for water sampling for chemical analysis are provided. The desired environments are maintained by chemical addition and by blowdown.

Figure 15 is an overall view of the loop. Most of the high temperature portions are insulated for thermal efficiency and safety. A detailed description of the loop facility is given in Ref. 7.

Fig. 15. Overall View of Corrosion Test Loop. The Large Vertically Oriented Vessels in the Center and Right Center Are the Model Test Vessels. The Test Rack for the Miniatures Is in the Left Rear

V. MINIATURE HEAT EXCHANGER TESTING

Miniature heat exchangers were fabricated, using the following tube materials: Type 304 stainless steel, Croloy 16-1, Inconel, Monel, nickel and bimetal (carbon steel secondary, stainless steel primary). Table 8 summarizes the materials of construction and test results for the miniature (and model) vessels. Appendix A gives the chemical composition of heat exchanger materials.

A. GENERAL DESCRIPTION

1. Design

The design of the first several miniature heat exchangers tested in this program is shown in Fig. 16. The secondary was static in the sense that there was no external circulation of the secondary environment. However, the condenser coil in the dome, which maintained the proper secondary pressure, produced a water-vapor-condensate cycle. Nine test vessels of this configuration were tested. These included three with AISI Type 304 stainless steel tubes, three with Croloy 16-1 tubes, one with bimetal tubes (low carbon steel on the secondary side) and two with Inconel tubes.

The test loop was extensively modified during the course of the program, which necessitated a design modification of the miniature test vessels. The secondary system was made dynamic. The design of the modified test vessel is shown in Fig. 17. Steam, generated in the secondary side of the test vessel, passes out through an overhead port, is condensed externally, and is returned to the vessel through a make-up tank and pump. The environmental constituents are controlled by blowdown or by additions of required chemicals injected into the secondary make-up water.

All the miniature test vessels were oriented horizontally so that the planes of the two hairpin tubes were oriented ±30° from the vertical. Water level was maintained so that half of each tube was exposed to each phase, vapor and liquid.

2. Fabrication Procedure

The heat exchanger unit consists of three main subassemblies: the tube and tube sheet assembly, the primary shell and the secondary shell. Two types of tube sheets are used; either the tube sheet is of a corrosion resistant alloy--possibly that of the tubing--or of carbon steel with the primary surface clad with a corrosion resistant alloy such as stainless steel, nickel or Inconel. The tube sheet of corrosion resistant

TABLE 8

Test Heat Exchanger Summary

Heat Exchanger Type	Number	Tube Material	Tube Sheet Material	Overlay	Shell Material	Water Conditions	Status
Miniature	MIN-1	304 SS	304 SS	308 SS	304 SS	4	Failed--42 hr
Miniature	MIN-2	304 SS	304 SS	308 SS	304 SS	5	Service--1390 hr
Miniature	MIN-3	304 SS	304 SS	308 SS	304 SS	6	Failed--1085 hr
Miniature	MIN-4	430-M (B W)	15 Cr, 0.17 Ni	430-M (B W)	16 Cr, 0.26 Ni	7	Failed--2578 hr
Miniature	MIN-5	430-M (B W)	15 Cr, 0.17 Ni	430-M (B W)	16 Cr, 0.26 Ni	8	Failed--941 hr
Miniature	MIN-6	430-M (B W)	15 Cr, 0.17 Ni	430-M (B W)	16 Cr, 0.26 Ni	9	Service--2767 hr
Miniature	MIN-7	Bimetal[a]	Carbon steel	308 SS	Carbon steel	4	Service--3256 hr
Miniature	MIN-8	Inconel	Inconel	Inco "A"	Inconel	10	Service--5296 hr
Miniature	MIN-9	Inconel	Inconel	Inco "A"	Inconel	11	Service--2631 hr
Miniature	MIN-10	Inconel	Inconel	Inco "A"	AISI-1030 CS	14	Service--3044 hr
Miniature	MIN-11	Inconel	Inconel	Inco "A"	AISI-1030 CS	15	Service--3024 hr
Miniature	MIN-12	Monel	AISI-1020 CS	Nickel	AISI-1030 CS		Not tested
Miniature	MIN-13	Monel	AISI-1020 CS	Nickel	AISI-1030 CS	15	Service--1393 hr
Miniature	MIN-14	Monel	AISI-1020 CS	Nickel	AISI-1030 CS	12	Service--1418 hr
Miniature	MIN-15	Bimetal[a]	AISI-1020 CS	---	AISI-1030 CS	16	Service--3019 hr
Miniature	MIN-16	Bimetal[a]	AISI-1020 CS	---	AISI-1030 CS	15	Service--3035 hr
Miniature	MIN-17	Nickel	AISI-1020 CS	Nickel	AISI-1030 CS		Not tested
Miniature	MIN-18	Nickel	AISI-1020 CS	Nickel	AISI-1030 CS	15	Service--1385 hr
Miniature	MIN-19	Nickel	AISI-1020 CS	Nickel	AISI-1030 CS	12	Service--1350 hr
Steam generator	MOD SG-1	304 SS	304 SS		304 SS	1	Service--1927 hr
Superheater	MOD SH-1	304 SS	304 SS		304 SS	1	Failed--1927 hr
Steam generator	MOD SG-2	Bimetal[a]	Carbon steel	308 SS	Carbon steel	1 (3)	Service--5041 hr
Superheater	MOD SH-2	Bimetal[a]	Carbon steel	308 SS	Carbon steel	1 (3)	Service--5041 hr
Steam generator	MOD SG-3	304 SS	304 SS		304 SS		Not tested
Superheater	MOD SH-3	304 SS	304 SS		304 SS		Not tested
Steam generator	MOD SG-4	Bimetal[a]	Carbon steel	308 SS	Carbon steel	13	Service--4836 hr
Superheater	MOD SH-4	Bimetal[a]	Carbon steel	308 SS	Carbon steel	13	Service--4836 hr
Steam generator	MOD SG-5	Croloy 16-1	A350LF-1	308 SS	Carbon steel	3	Service--4253 hr
Superheater	MOD SH-5	Croloy 16-1	A350LF-1	308 SS	Carbon steel	3	Service--4253 hr
Steam generator	MOD SG-6	Inconel	AISI-1020 CS	Inco "A"	Carbon steel	3	Service--3815 hr
Superheater	MOD SH-6	Inconel	AISI-1020 CS	Inco "A"	Carbon steel	3	Service--3815 hr
Steam generator	MOD SG-7	Inconel	AISI-1030 CS	Inco "A"	AISI-1030 CS	12	[illegible]
Superheater	MOD SH-7	Inconel	AISI-1030 CS	Inco "A"	AISI-1030 CS	12	Service--[illegible]

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Miniature	MIN-14	Monel	AISI-1020 CS	Nickel	AISI-1030 CS	12	Service-- [illegible]
Miniature	MIN-15	Bimetal(a)	AISI-1020 CS	---	AISI-1030 CS	16	Service--3019 hr
Miniature	MIN-16	Bimetal(a)	AISI-1020 CS	---	AISI-1030 CS	16	Service--3035 hr
Miniature	MIN-17	Nickel	AISI-1020 CS	Nickel	AISI-1030 CS		Not tested
Miniature	MIN-18	Nickel	AISI-1020 CS	Nickel	AISI-1030 CS	15	Service--1385 hr
Miniature	MIN-19	Nickel	AISI-1020 CS	Nickel	AISI-1030 CS	12	Service--1350 hr
Steam generator	MOD SG-1	304 SS	304 SS		304 SS	1	Service--1927 hr
Superheater	MOD SH-1	304 SS	304 SS		304 SS	1	Failed--1927 hr
Steam generator	MOD SG-2	Bimetal(a)	Carbon steel	308 SS	Carbon steel	1 (3)	Service--5041 hr
Superheater	MOD SH-2	Bimetal(a)	Carbon steel	308 SS	Carbon steel	1 (3)	Service--5041 hr
Steam generator	MOD SG-3	304 SS	304 SS		304 SS		Not tested
Superheater	MOD SH-3	304 SS	304 SS		304 SS		Not tested
Steam generator	MOD SG-4	Bimetal(a)	Carbon steel	308 SS	Carbon steel	13	Service--4890 hr
Superheater	MOD SH-4	Bimetal(a)	Carbon steel	308 SS	Carbon steel	13	Service--4890 hr
Steam generator	MOD SG-5	Croloy 16-1	A350LF-1	308 SS	Carbon steel	3	Service--4253 hr
Superheater	MOD SH-5	Croloy 16-1	A350LF-1	308 SS	Carbon steel	3	Service--4253 hr
Steam generator	MOD SG-6	Inconel	AISI-1030 CS	Inco "A"	Carbon steel	3	Service--3819 hr
Superheater	MOD SH-6	Inconel	AISI-1020 CS	Inco "A"	Carbon steel	3	Service--3819 hr
Steam generator	MOD SG-7	Inconel	AISI-1030 CS	Inco "A"	AISI-1030 CS	12	Service--4747 hr
Superheater	MOD SH-7	Inconel	AISI-1030 CS	Inco "A"	AISI-1030 CS	12	Service--4747 hr

NOTES:

(a) Primary side--Type 304 SS (0.030 in.)
Secondary side--carbon steel (0.035 in.)

1. Chloride--40 to 50 ppm
Phosphate--40 to 80 ppm
Sulfite--6 to 10 ppm
pH--10.5 to 10.8

2. To be determined

3. Cl--800 to 1000 ppm
O_2--none (controlled with sodium sulfite)
pH--8.3 to 9.5 with PO_4

4. Chloride--991.6 ppm
Phosphate--61 ppm
O_2--40 ppm
pH--10.5

5. Chloride--995.3 ppm
Phosphate--58 ppm
O_2--7.89 ppm
pH--10.5

6. Chloride--108.5 ppm
Phosphate--none
O_2--7.85 ppm
pH--11.5

7. Chloride--800 ppm
Phosphate--50 ppm
O_2--21% by volume
pH--10.5

8. Chloride--800 ppm
Phosphate--none
O_2--21% by volume
pH--10.5

9. Chloride--400 ppm
Phosphate--none
O_2--10% by volume
pH--6.5

10. Chloride--1000 ppm
O_2--air sat. water, air as cover gas
pH--8.3 to 9.5 with PO_4 water treat

11. Chloride--1000 ppm
O_2--air sat. water, air as cover gas
pH--8.3 to 9.5 with NaOH
PO_4--none

12. Chloride--0.5 ppm max
Phosphate--150 ppm
Sulfite--10 ppm
pH--10 to 10.5

13. Chloride--0.5 ppm max
Sulfite--10 ppm
Total solids--200 ppm max
pH--8.5 (PO_4)

14. Chloride--1000 ppm
pH--10 (NaOH)
O_2--no treatment*

15. Chloride--1000 ppm
pH--10 (33% Na_3PO_4 and 67% Na_2HPO_4)
O_2--no treatment*

16. Chloride--800 ppm
pH--10 (33% Na_3PO_4 and 67% Na_2HPO_4)
O_2--no treatment*

*The secondary makeup tank will be maintained at 180° F, open to the atmosphere, which will maintain the oxygen concentration at somewhat less than 0.5 ppm.

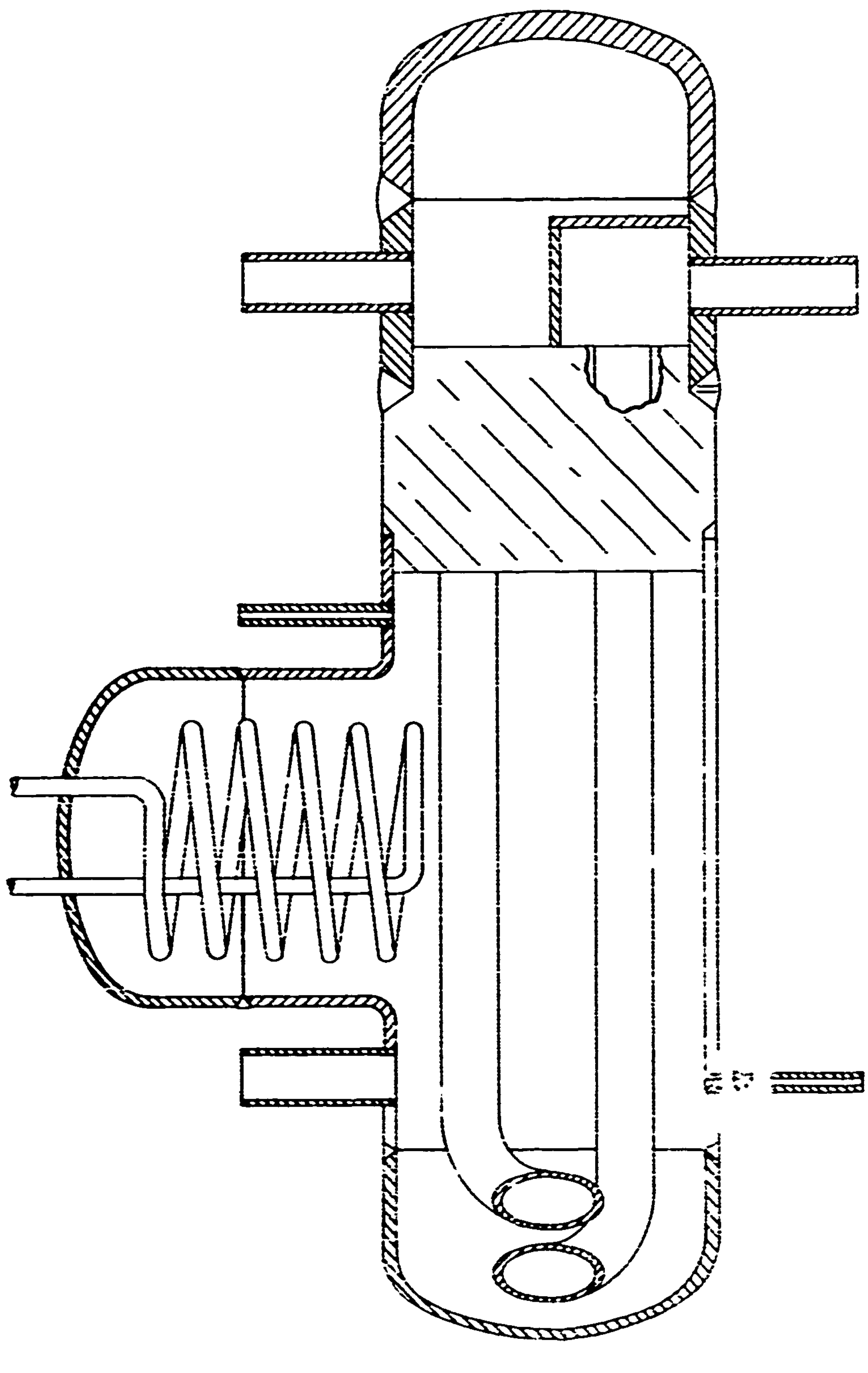


Fig. 16. Design of Static Miniature Heat Exchanger

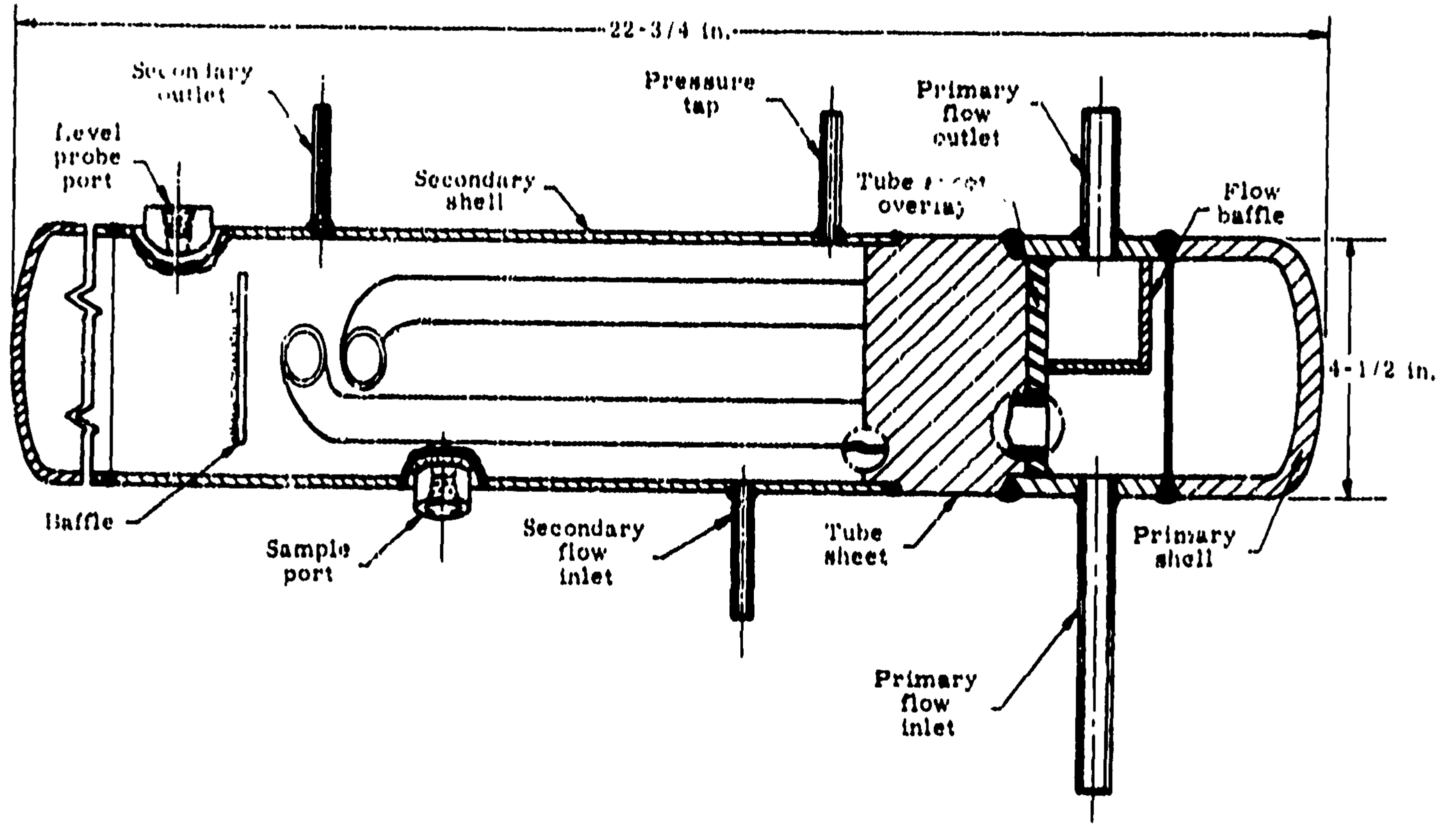


Fig. 17. Design of Dynamic Miniature Heat Exchanger

alloy is machined completely before further assembly. In the case of the carbon steel tube sheet, the primary surface is weld-clad before machining if an alloy tubing is used and after machining if a bimetal tube of carbon steel and stainless steel is used.

For the preclad tube sheet, a weld clad of 3/8-inch thickness is deposited on the unmachined blank. The surface is machined, leaving 1/4-inch thickness of clad. The blank is then machined to final dimensions. The tubes are inserted into the drilled holes of the tube sheet and are rolled in place, producing approximately 5% reduction in the tube wall thickness. The tube is expanded about 1/4 inch beyond the tube sheet. The tube ends are positioned either flush with the tube sheet surface of 1/16 inch above the surface. The tube-to-tube sheet seal weld is produced by the TIG process with no filler metal added.

For the post-clad tube sheet, the surface to be clad is machined 1/4 inch below the finish dimension to provide for the clad. The bimetal tubes have the outer layer of carbon steel machined away for approximately 1/2 inch at the ends. The ends are inserted into the holes in the tube sheet and are positioned so that the edge of the carbon steel clad extends approximately 1/16 inch above the tube sheet surface. The tubes are rolled in place, with a 5% reduction in the tube wall thickness. The tube is expanded 1/4 inch beyond the tube sheet. The carbon steel clad is weld-joined to the tube sheet by the metallic arc process, using a carbon steel weld electrode. With copper chill plugs inserted in the tube ends, a layer of stainless steel is deposited around each tube by the TIG process. The tube sheet surface is clad by the metallic arc process and each successive layer of clad is initiated by first making a fillet weld around each tube. The total clad layer is made 3/8 inch thick and is machined to provide a final thickness of 1/4 inch.

The primary shell components are fabricated from a 300 series stainless steel and are generally assembled by making a TIG weld root pass at each joint and filling in by the metal arc process. A fillet weld of Inconel joins the shell and the tube sheet clad, thus preventing the carbon steel from contacting the primary water. The flow baffle is joined to the tube sheet and the shell with Inconel fillets. The end cap weld is the final closure of the primary chamber. This butt weld is made with stainless steel weld metal.

The secondary shell is constructed entirely of carbon steel, except in Vessels 1, 2 and 3, and is complete when joined to the tube sheet. The junction weld between these two components is made by the metal arc process with low alloy steel filler metal. The units are not heat treated.

The completed miniature heat exchangers were pressure tested and checked for leaks under water. The primary side was pressurized with air to 2260 psi and the secondary side to 375 psi. The vessels were cleaned with 10 oz/gal Oakite 90 and rinsed well, prior to installation in the loop. They were recleaned after installation in the corrosion loop.

3. Pretest Evaluation

The tubing, tube sheet, secondary shell, and weld wire are analyzed chemically to establish compliance with material specification. The tubing is examined metallographically for reference in the post-test evaluation.

4. Post-Test Evaluation

At the completion of the corrosion test, the heat exchangers are sectioned for examination. The primary and secondary shells are removed from the tube and tube sheet assembly by cutting through each close to the tube sheet surface. Care is taken here to prevent damage to the tubes and the adhering corrosion products. Photographs are taken to record the general appearance of the units. Macrophotographs of pertinent areas are also taken.

Corrosion products are scraped from the tube surfaces and examined by X-ray diffraction to determine the composition of the corrosion products. Wet analyses and emission spectroscopy analyses are run when necessary to determine the major constituents of the corrosion products. The tube sheet assembly is sectioned further for metallographic examination. The locations from which metallographic specimens and specimens for visual checks are taken and the details to be examined are outlined below.

(1) Tube-to-tube sheet weld joints. Longitudinal sections of all of the tube welds examined to observe:

(a) Heat affected zone of the primary tube sheet surface.

(b) Weld surface--primary side.

(c) Heat affected zone of tube wall--primary surface.

(d) Heat affected zone of tube wall--secondary surface, if in contact with water.

(e) Weld proper--determine soundness and general weld characteristics.

(2) Tube crevice surfaces are exposed by the removal of half-tube sections to observe:

(a) Depth of penetration of secondary water into crevice.

(b) Presence of cracks as determined by liquid penetrant test.

(3) Longitudinal metallographic sections are made from each of the tube-to-tube sheet crevice areas, one-half inch into the crevice from the secondary surface to examine:

(a) The crevice surfaces.

(b) Surface of tube sheet adjacent to the hole.

(4) Tubes and tube bends. The following sections are taken from each tube for metallographic examination and determination of the effects of the secondary environment.

(a) Straight portion of tube exposed to secondary water.

(b) Straight portion of tube exposed to vapor, where applicable.

(c) Section of tube at point of maximum bending.

(d) Contact line between water and vapor--transverse to water line, where applicable.

(5) Tube sheet periphery--representative number of metallographic specimens are taken at the secondary corner and at the shell-to-tube sheet weld.

(a) Transverse specimen at water-to-vapor interface, where applicable.

(b) Machined OD of tube sheet near secondary surface.

(c) Weld joining shell to periphery of tube sheet--determine weld soundness and general characteristics.

(d) Surfaces adjacent to weld if in contact with water.

Following is an outline of the general heat exchanger sectioning procedure:

(1) Remove shells by sectioning close to tube sheet surfaces.

(2) Cut through tubes approximately 1/4 inch above tube sheet surface.

(3) Cut through tube sheet along holes; section through all holes.

(4) Transverse cuts through half-tube sections approximately 1/4 inch from weld to allow for removal of tubes to expose crevice surfaces.

(5) Preparation of metallographic specimens from specific areas as detailed.

B. TESTS WITH AISI TYPE 304 STAINLESS STEEL VESSELS, (MIN 1, 2 and 3)

These three corrosion test vessels were constructed entirely of Type 304 stainless steel with Type 308 filler metal for all welds. The hairpin tubes were fabricated from a single length of tubing with a 3/4-inch OD and a 0.065-inch wall. These vessels were tested statically.

1. Tests and Results

a. MIN 1

MIN 1, with a total secondary volume of 2.85 liters, was charged with 0.83 liter of water containing 992 ppm Cl, 61 ppm PO_4 and 40 ppm dissolved oxygen. The resulting pH was 10.5. Fifty and a half milliliters of air were added to the system. If all the oxygen in the system were in the vapor space, its concentration would be 1.68%. However, according to Henry's Law, about 1.1 ppm O_2 was dissolved in the water at the operating temperature of the secondary water, which was 194° C.

MIN 1 failed after 42 hours. Examination revealed large cracks in the tubes which had been submerged in water. These cracks are clearly visible to the unaided eye, as shown in Fig. 18. The cracks extended through the entire thickness of the tube wall, as shown in Fig. 19. The cold worked condition of the tubing is shown by the strain lines visible in Fig. 19. All the cracks originated at the outside surface of the tubes. MIN 1 had also developed stress corrosion cracks around each hole of the submerged portion of the tube sheet. The cracks appeared to originate at the sharp edges of the drilled holes and propagate in planes radial to the hole axis.

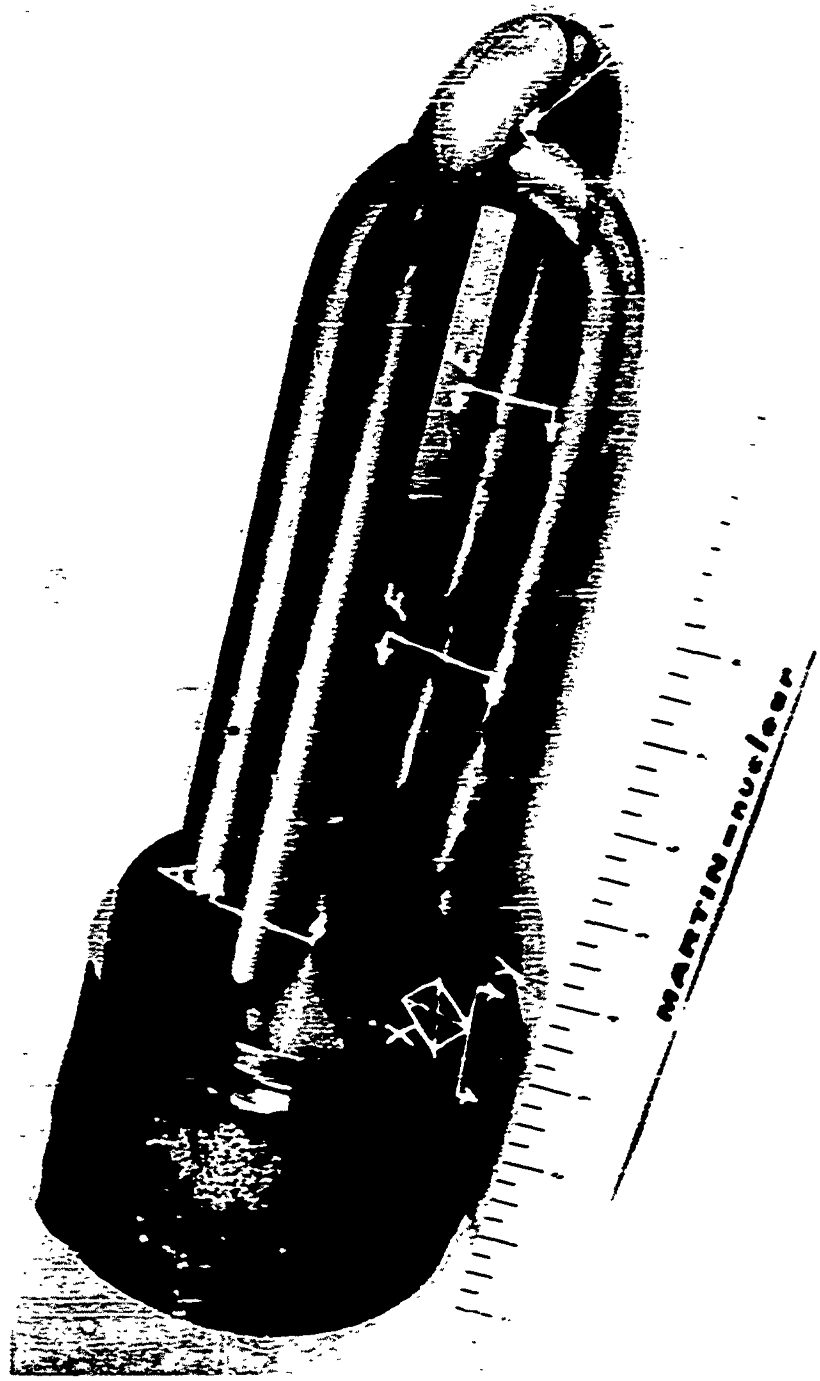


Fig. 18. View of Secondary Surfaces of MIN 1. The Cracks Occurred in the Submerged Tubes

Fig. 19. Photomicrograph of MIN 1, Area "F" of Fig. 16 The Full Tube Thickness Was Penetrated. The Narrow End of the Crack Is at the ID Magn 100x

Fig. 20. Closeup of Submerged Portion of Tube Sheet of MIN 3. Note Cracks Radiating from Machined Holes Magn 3x

b. MIN 2

MIN 2, with a total secondary volume of 2.85 liters, was charged initially with 0.83 liter of water containing 995 ppm Cl, 58 ppm PO_4 and 7.9 ppm dissolved oxygen. The resulting pH was 10.5. No additional oxygen was added to the system, but the vapor space was filled to one atmosphere with argon. If all of the oxygen present were considered to be in the atmosphere, the concentration would be about 0.23%. In this case, Henry's Law shows that less than 0.2 ppm O_2 was dissolved in the water at operating temperature. This system was cooled down and recharged every 100 hours with fresh solution corresponding roughly to the initial charge water. This miniature was in service 1890 hours and it did not fail.

At the conclusion of the test the secondary surfaces, excluding tube-to-tube sheet crevice surfaces, was free of any measurable quantities of foreign matter and showed only discoloration of the submerged surfaces. The tube-to-tube sheet joints with expanded tubing showed no penetration by the environmental medium. The joints which did not have expanded tubing were similar in appearance, above or below the water line, but there was some discoloration of mating surfaces.

c. MIN 3

MIN 3, with a total secondary volume of 2.85 liters, was charged with 0.83 liter of water containing 108 ppm Cl, no phosphates and 7.9 ppm dissolved oxygen. The pH was adjusted to 11.5 with NaOH. No additional oxygen was added to the system, but the vapor space was brought to one atmosphere with argon. As in the case of MIN 2, the calculated oxygen dissolved in the environmental water was less than 0.2 ppm at operating temperature. Under those conditions, MIN 3 failed after 1065 hours.

Examination of MIN 3 showed that the tube-to-tube sheet crevices of the unexpanded tube contained rather heavy deposits of salt. In addition, the machined holes of the tube sheet showed local pitting on the surfaces, which was more extensive in the hole exposed to vapor. Cracks developed in submerged portions of both tubes and tube sheet, also in the unexpanded tube and the tube sheet which formed the crevice exposed to vapor, where pitting had occurred. Large axial cracks were present in the bent portion of one tube. All the cracks in the tube originated at the outside surfaces, and some penetrated the entire wall thickness. Cracking occurred also in the submerged portion of the tube sheet in the area adjacent to the tube holes, as shown in Fig. 20. A network of very shallow stress corrosion cracks developed at the mating surfaces of the tube and tube sheet near the weld of the steam phase unexpanded tube-to-tube sheet joint. These cracks developed in the heat affected zones of the parent materials.

2. Analysis of Results

MIN 1 and MIN 2 provide an interesting contrast, i.e., the only difference in environmental exposure was the difference between about 1.1 ppm dissolved oxygen in the water of MIN 1 and 0.2 ppm dissolved oxygen in the water of MIN 2. MIN 1 failed, but MIN 2 did not. The absence of cracks in MIN 2 strongly suggests that a low concentration of oxygen, even if periodically depleted and replenished, is tolerable. Perhaps the presence of phosphate combined with low oxygen is responsible. The cracking in MIN 3 is attributed to the concentration of chloride in the crevices. The absence of phosphate and the presence of free alkali may be significant also. All of the cracking was transgranular. The incidence of cracking was greatest in the submerged areas of the test vessels. The major danger area in contact with the steam phase was the tube-to-tube sheet junction. Cracking was limited to the outside surface of the tubing and the edges of the machined holes in the tube sheet. Residual stresses produced in the tubes during manufacture were the primary source of stresses contributing to tube failures. The failures of the tube sheets around the drilled holes can be attributed to a highly stressed condition resulting from residual stresses in the stock and intensification of these stresses because the machined holes act as stress raisers. No corrosion or cracking occurred in the expanded tube-to-tube sheet junctions because there was no penetration by the environmental medium.

Since stress corrosion cracking occurred in the tubing, a cursory analysis of the existing stresses in the tubes was made. Figure 21 shows three short lengths of tubing, the outer two of which were cut through one side with an abrasive cutting disk, while the center piece was cut only half way to show the width of the cut. The pieces which were cut through sprang apart about 1/32 inch after cutting. It is evident that there were circumferential tensile stresses of considerable magnitude in the tubing.

C. TESTS WITH CROLOY 16-1 VESSELS (MIN 4, 5 AND 6)

The Croloy 16-1 tubing used in MIN 4, 5 and 6 was 0.75 inch outside diameter with an 0.065-inch wall thickness. The tube sheet was made from Type 430 stainless steel bar stock. The material did not meet chemical specifications due to the presence of 2.45% Mo. It was found necessary to use this material, however, since it was the only stock available in the required size at the time these units were fabricated. Difficulties attributable to the application of this material arose when the tube-to-tube sheet welds were made. A consistent pattern of radial cracks occurred throughout all of the seal welds.

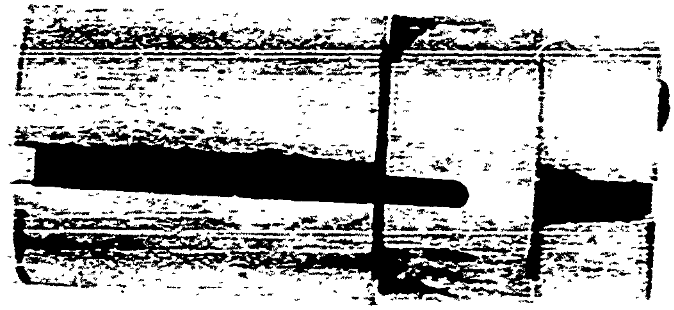


Fig. 21. Longitudinal Cuts in Tubing, Illustrating the Magnitude of Stresses in the Tubing (3x Mag)

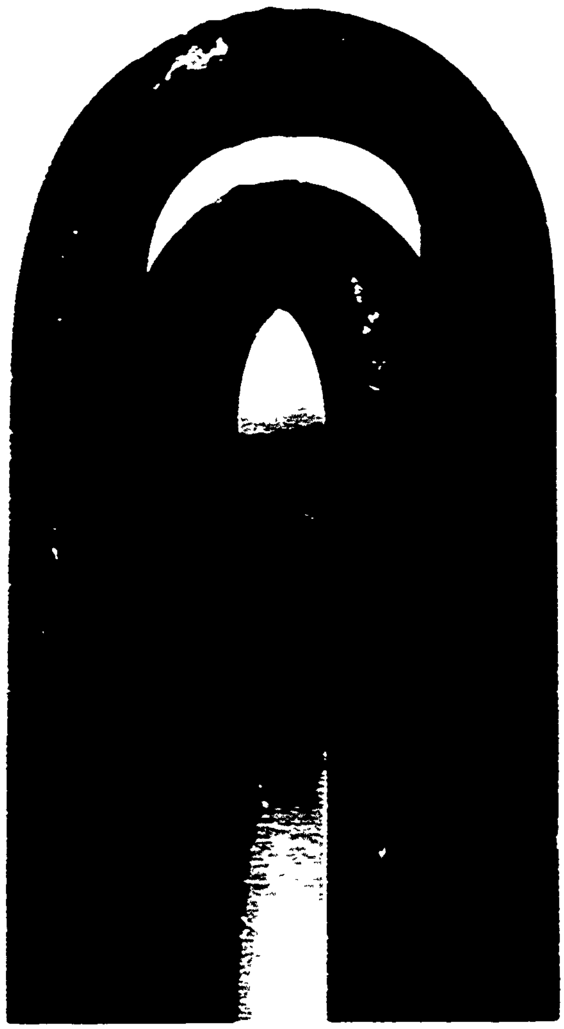


Fig. 22. Close-up of Tubes and Interface

The defective joints were repaired by machining out the fused material and rewelding with Inco-Weld A electrodes. The inert gas tungsten arc process was used to make these repairs and the initial seal welds. Helium leak checks of the repaired tube sheet assemblies disclosed no leaks. The Type 304 stainless steel primary shell and the Type 430 stainless steel secondary shell were joined to the tube sheet with Inco-Weld A material.

1. Tests and Results

a. MIN 4

MIN 4 was charged with 0.85 liter of water that contained 763 ppm Cl and 51 ppm PO_4. The resulting pH was 10.7. Air at atmospheric pressure was the covergas. According to Henry's Law, the initial concentration of oxygen dissolved in the water at operating temperature, 381° F, was about 12 ppm. The vessel had performed satisfactorily for 2091 hours when a decrease in pressure was noted. An unsuccessful attempt was made to increase the pressure by decreasing the flow of cooling water through the coil in the secondary system. With the cooling water valve opened slightly, pressure was maintained at 175 psi for the next several days until the pressure dropped off to about 150 psi at 2283 hours. The pressure finally dropped to about 125 psi at 2578 hours and the test was discontinued.

After the shell was removed, the tubes appeared as shown in Fig. 22. The entire secondary was evenly coated with a dark, almost black, adherent deposit which was identified as Fe_2O_3 by X-ray diffraction. A heavy deposit of red rust appeared as a ring at the vapor-water interface on all secondary surfaces. A metallographic section of a submerged tube taken about 1/4 inch from the tube sheet showed that the scale was about 0.2 mil thick and was a uniform deposit. Some pits were noted at this point, but they did not exceed 0.5 mil in depth. A metallographic section of the tube sheet from one of the crevice areas adjacent to the tube-to-tube sheet weld of an unrolled tube showed a few very slight cracks (see Fig. 23). These cracks were at the edge of the heat affected zone. It is possible that the molybdenum in the tube sheet was responsible for the cracks.

An area of great concern and interest is the vapor-water interface where the corrosion products were deposited. Examination of this area showed pits up to about 10 mils in depth under the deposit.

The cause of the leak in MIN 4 was not found; presumably, it was in the vapor space of the secondary, because no crystallized NaCl was visible on the outside of the vessel below the waterline. No leaks occurred between the primary and secondary.

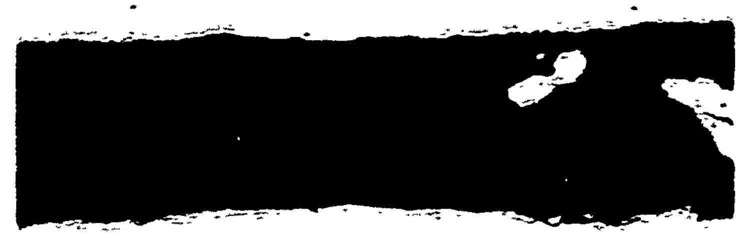


Fig. 23. MIN 4--Section of Tube Sheet at Crevice of Unrolled Tube, as Polished. Note Cracks

Fig. 24. Section Taken from Secondary Side Tube Exposed to Steam Phase--Worst Case of Pitting Seen in MIN 4 or MIN 5

b. MIN 5

MIN 5 was charged with 0.85 liter of water containing 795 ppm Cl at pH 10.5 adjusted with NaOH. Air at atmospheric pressure was the covergas. As was the case with MIN 4, Henry's Law indicated that the dissolved oxygen at operating temperature was about 12 ppm. The vessel performed satisfactorily for about 480 hours; then the pressure started to decrease. An unsuccessful attempt was made to increase pressure by decreasing the flow rate of the cooling water. Increased primary flow had no effect.

The vessel was removed from test and pressurized with air to 150 psi under water. The leak was located in a secondary shell weld. The weld in that area was ground out and rewelded. The vessel was recharged with water of the original composition and testing was resumed. At 733 hours, the unit again lost pressure. The leak was located by pressurizing hydrostatically to 500 psi. Again the leak was in a secondary weld. Repairs were made, the vessel recharged and again placed in test. At 885 hours, the pressure again started to drop and continued slowly until it reached 125 psi at 941 hours. The test was discontinued.

At the conclusion of the test, an attempt was made to sample the vapor space and the charge water. However, it was found that only a few milliliters of the charge water remained.

When the secondary shell was removed no prominent ring of corrosion products was found as in MIN 4. Instead, the deposit was distributed over a large vertical area on the tube bends presumably because of the fluctuating vapor-water interface level caused by the three leaks.

The interior of the secondary shell presented much the same appearance as MIN 4. The dark adherent deposit consisted of Fe_2O_3 as before. Again, the layer of corrosion products was very thin (about 0.2 mil). Figure 24 is a cross section from the outer circumference of one of the tubes at the interface. The area was the worst of either MIN 4, MIN 5 or MIN 6, so far as pitting was concerned. The approximate depth of the pits is 10 mils.

Metallographic sections were made of the tube-to-tube sheet area adjacent to the seal weld in all the tubes. An interesting result was discovered. The heat affected zone of the tube sheet of the unrolled tube was extensively cracked. A series of polishings on one of the specimens, each polishing removing about 1/64 inch, showed that the cracking was rather extensive. The explanation of these cracks can probably be traced to the molybdenum in the tube sheet composition. As was found in the case of MIN 4, the secondary environment penetrated the unrolled tube-to-tube sheet crevice, but was excluded from the rolled tube. The leak, presumably in the secondary shell, was not found.

c. MIN 6

MIN 6 was charged with 0.98 liter of water that contained 403 ppm Cl. The pH, unadjusted, was 6.5. The pressure of the secondary vapor space was reduced to 14.2 inches of mercury and sealed. The resulting partial pressure of oxygen caused about 6 ppm O_2 to be dissolved initially in the water at the operating temperature. The vessel performed satisfactorily over its test life of 2767 hours.

When MIN 6 was examined after the tests, it was found that the submerged tubes were evenly coated with a dark, almost black, oxide. The vapor phase tubes were coated with an oxide from various degrees of iridescence (almost no oxide film) to very dark where condensed water dripped onto the exposed tubes. There was no prominent interface. There were a few small isolated areas of red iron rust on the submerged tubes. X-ray diffraction analysis showed that magnetic iron oxide, Fe_3O_4, was the only prominently discernible pattern. It is interesting to note that the dominant iron oxide structure was Fe_3O_4, whereas in MIN 4 and MIN 5, the dominant structure was Fe_2O_3. MIN 6 had a more limited supply of oxygen initially. Both MIN 4 and MIN 5 had more oxygen initially and had leaks. During the period when pressure could not be maintained on these vessels, a power outage and a primary loop heater failure interrupted the tests. This provided ample opportunity for oxygen to be drawn into the secondary as the vessels cooled. In addition to this, MIN 5 was charged three times during its test life, and each time the oxygen was replenished. Therefore, it is indicated that the initial low oxygen concentration made the test on MIN 6 appear favorable. No cracks were found in this test vessel.

2. Analysis of Results

The performance of the Croloy 16-1 tubes was encouraging in that none of the tubes cracked. Although it was impossible to maintain continuous tests with two of the three Croloy 16-1 test vessels, the fault lay with the shell closure welds, not the tubes. Initially, the tube-to-tube sheet seal welds leaked due to cracks which were repaired prior to testing. On the basis of the test of these miniature vessels with static secondary systems, the Croloy 16-1 tubes performed satisfactorily. The limitation of the static system as a test device, without replacement of oxygen, is indicated by the formation of Fe_3O_4 in MIN 6, the only Croloy 16-1 miniature which did not leak. As expected, the worst corrosion, i.e., the deepest pits, occurred at the vapor-to-water interface.

D. TEST WITH BIMETAL VESSEL (MIN 7)

The bimetal tubing, 0.750-inch OD by 0.065-inch wall, used in this test vessel had a clad of 1000 series carbon steel over a Type 304 stainless steel liner. The tube sheet was machined from a 4-1/2-inch OD bar of annealed SAE 1020 carbon steel. It had provisions for the deposition of a stainless steel weld on the primary face and adjacent periphery. The surfaces to be clad were undercut 1/4 inch. The overlay was deposited to a thickness in excess of the finished dimensions to allow for final machining. The clad surfaces were machined and the tube entrance holes were drilled and reamed to size, 0.005 inch over the tube OD. The holes were counterbored on the clad side to a depth sufficient to remove the stainless steel overlay. The counterbore was 1-1/8 inch in diameter. This provided a 3/16-inch ferritic steel land around the tubes. The bimetal tubes were bent, machined to length and inserted in the tube sheet. The squared ends of the tubes were positioned to project 1/16 inch above the bottoms of the counterbored surfaces and were roller expanded into the tube sheet.

The tubes were joined to the tube sheet with an Inconel weld so placed that only the outer ferritic layer of the tube was penetrated. The remaining counterbore volume was filled in with Type 308 stainless steel weld metal. The Inconel was thus overlaid with stainless steel and a junction made between the stainless steel layer of the tube and the primary surface clad. The excess buildup in the tube was removed by reaming. After the containment shells were joined to the tube sheet by peripheral welds, the unit was inspected with dye penetrant and statically tested with 2260 psi on the primary circuit and 375 psi on the secondary.

1. Tests and Results

MIN 7 was charged with water containing 1000 ppm Cl and 50 ppm PO_4 at pH 10.5 with 1.6% O_2 in the vapor space, initially. It was tested 3256 hours with an interim down time of 138 days. The secondary system was untouched during this entire period. At the end of the test period, all the oxygen was depleted from the secondary environment. All indications were that the bimetal miniature test could have continued indefinitely.

The secondary surfaces were coated with a dense, adherent dark film similar to that found in all the other test units. X-ray examination showed the film to be composed of alpha-Fe_2O_3 and Fe_3O_4. Figure 25 shows the tubes with the corrosion products as removed from the shell. Examination of the secondary tube and tube sheet surfaces revealed no evidence of cracks, as expected.

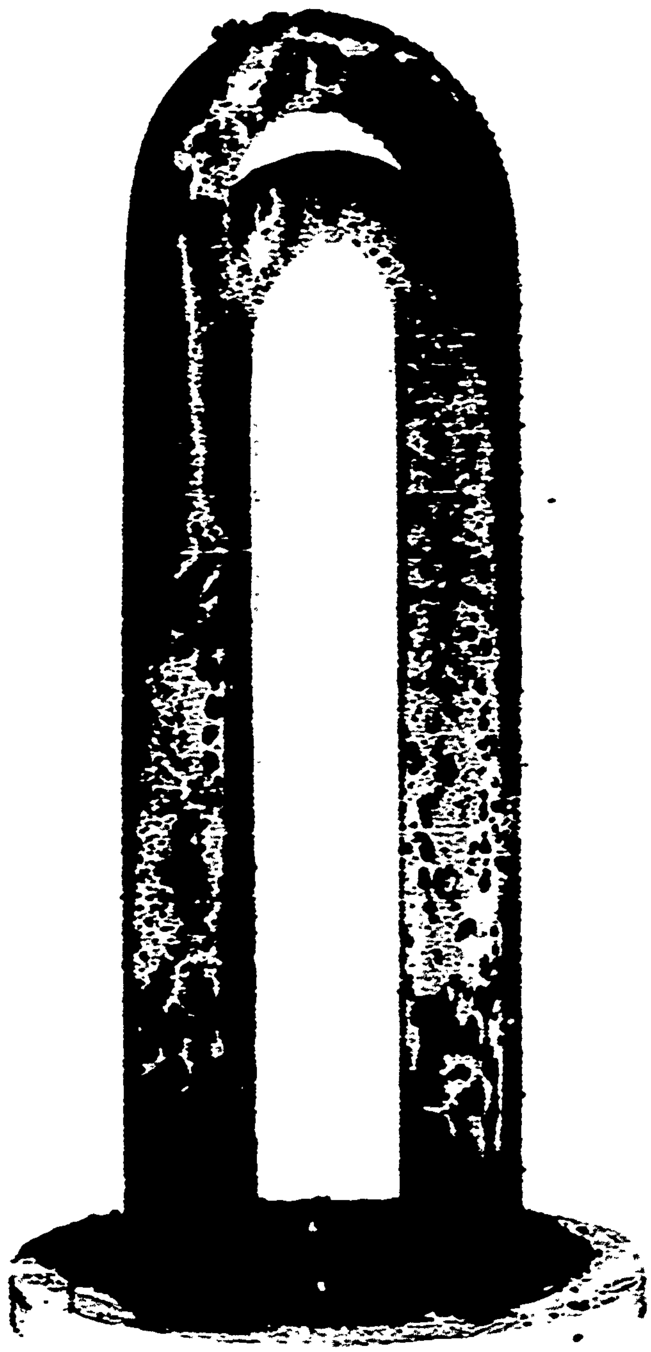


Fig. 25. MIN 7 with Secondary Shell Removed

Micro examination of the tubing revealed numerous irregularities in one of the two tubes. The stainless steel was approximately 1/4 of the tube wall thickness instead of the usual 1/2 value. It was highly sensitized along the entire tube length, and cracks were present which completely penetrated the Type 304 stainless steel liner, following intergranular paths as shown in Fig. 26. An unusually broad zone of heavy carbide concentration can be seen in the stainless steel at the carbon steel interface. Both the carbon and stainless steel contained unusually high percentages of carbon. The high carbon content of the stainless steel can be attributed to the diffusion of carbon from the ferritic steel during tube fabrication. The intergranular cracks are assumed to have developed during fabrication of the tubing as a result of the high carbon content. The cracks could not have resulted from corrosive attack since general grain boundary attack did not occur and the cracks are relatively uniform in width throughout their lengths. Additional material in the "as received" condition was not available for checking to determine if the cracks existed in the tubes before test.

2. Analysis of Results

The feasibility of using a low carbon clad in the secondary system, where only limited amounts of oxygen are present, was shown to be favorable. The known quantity of oxygen initially present was quickly used, after which no corrosion occurred. The key to a successful application is the elimination of oxygen.

E. TESTS WITH INCONEL VESSELS (MIN 8, 9, 10 AND 11)

The Inconel tubing used in these units was 3/4-inch outside diameter with an 0.070-inch wall thickness. The butt and fillet welds between the Inconel tube sheet and the Type 304 stainless steel primary were made with Inco-Weld A rod. In MIN 8 and 9, the secondary shell and tube sheet were both of Inconel and were joined with Inco-Weld A rod. These two vessels were tested with static secondaries. The secondary system in MIN 10 and 11 was dynamic; and the modified design, shown in Fig. 17, was used for these vessels. MIN 10 and 11 were fabricated with AISI 1030 carbon steel secondary shell joined to the Inconel tube sheet with Inco-Weld A rod.

Fig. 26. Intergranular Cracking in Type 304 SS Clad of Bimetal Tube Containing Numerous Irregularities (MIN 7) Magn 250x

1. Tests and Results

a. MIN 8

MIN 8 was charged with 0.77 liter of water that contained 1002 ppm chloride as Cl at pH 8.3 adjusted with trisodium phosphate. Air at atmospheric pressure was the covergas. The oxygen initially dissolved in the water at operating temperature was about 12 ppm. The vessel performed satisfactorily over its test life of 5296 hours. At the conclusion of the test, 0.77 liter of the charge water was recovered. The vapor space oxygen measured about 20% by volume. The pH was 8. Some crystallization of NaCl occurred at the interface and in the crevices of the unrolled tubes and thus lowered slightly the concentration of dissolved Cl.

The submerged tubes of MIN 8 were evenly coated with a very thin iridescent oxide film, as shown in Fig. 27. The tubing exposed to vapor had an oxide film thickness which varied from virtually none through various shades of iridescence to a heavier blue coloration where condensed water dripped onto the exposed tubes. There was a limited deposit of corrosion products at the interface. The overall appearance was excellent. As usual, the crevices between the tube and tube sheet of the unrolled tubes were partly filled with environmental solids. However, no deleterious effect was noted. There was not enough corrosion product to determine a thickness. Despite the fact that considerable oxygen remained after the test (about 20% volume), very little corrosion occurred.

b. MIN 9

MIN 9 was charged with 0.85 liter of water that contained 997 ppm chloride as Cl. The pH was adjusted to 8.3 with NaOH. Air at atmospheric pressure was the covergas. The initial concentration of oxygen in the water at operating temperature was about 12 ppm. The vessel performed satisfactorily over its test life of 2631 hours. At the conclusion of the test, 0.84 liter of the charge water was recovered. The vapor space oxygen measured about 16% by volume.

The visual appearance of MIN 9 contrasted sharply with the appearance of MIN 8. Figure 28 shows the unit with the secondary shell removed. The pale yellow-green film on the submerged portion of the tubes was less than 0.1 mil in thickness. X-ray diffraction identified two dominant structures in the film from the submerged tubes--a distorted $NiO \cdot H_2O$ structure with traces of Fe_2O_3. The portions of the tubes exposed to vapor had very little corrosion film except at the point where water, condensed by the cooling coil, dripped onto the tubes. Some areas of the tubes showed bright metal. A metallographic cross section of the submerged tube, after cleaning, showed some isolated areas of slight pitting in the range of 1 to 2 mils in depth. Environmental solids were again found in the crevices of the unrolled tube.

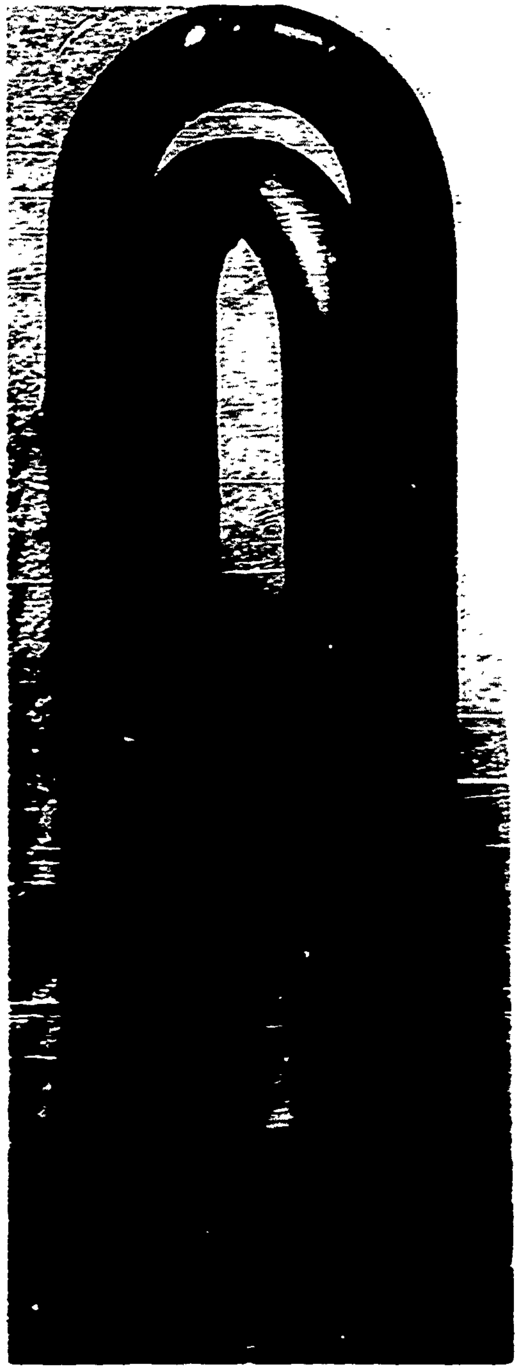


Fig. 27. Overall View of MIN 8 with Shell Removed

Fig. 28. Overall View of MIN 9. Note Pale Yellow-Green Film on Submerged Portion of Tubes

The general appearance of MIN 9 was very good. There was very little corrosion product in the secondary, neither on the tubes nor the Inconel secondary shell. The interior of the secondary shell exposed to vapor remained especially bright and lustrous.

The mechanism for the formation of the film is problematical. Presumably, the caustic was responsible. It is notable that no similar film occurred in MIN 8, where the pH was adjusted to the same level with trisodium phosphate. It is also interesting to note that, although ample oxygen remained at the conclusion of the test (at least 16% by volume), little corrosion occurred.

c. **MIN 10**

The secondary environment of MIN 10 contained 1000 ppm Cl and the pH was maintained at 10 with sodium hydroxide. There was no chemical treatment to remove oxygen but the secondary make-up tank was maintained at 180° F to expel dissolved gases. This maintained the oxygen concentration at somewhat less than 0.5 ppm. Since very impure conditions were used for the test environment, tap water was used for make-up. Three other miniature heat exchangers, MIN 11, 15 and 16, were tested along with MIN 10; and some difficulty was encountered in maintaining the specified water conditions. Chloride fluctuation was primarily caused by ineffective removal by the steam separators of entrained droplets which contained dissolved solids from the steam. This resulted in carry-over of the chemicals to the common storage tank. Since all the test vessels did not have the same steaming rate, there was some interchange of environmental solids. MIN 10 was tested 3044 hours without failure.

Figure 29 shows the tubes before they were cleaned. The tubes were covered with a rather loosely adherent boiler scale. Samples of the deposit on the tubes were removed from both the water and vapor phases. X-ray diffraction showed that $CaSO_4$ was the major constituent and $CaCO_3$ was the minor constituent in the deposit from both the vapor and liquid phases. Baltimore City tap water was used for make-up water because an objective of the tests was to further investigate the possibility of using untreated ground water in the secondary system of steam generators for plants at remote sites. The use of tap water accounts for the heavy boiler scale. The pale yellow-green film which appeared on the submerged portions of the tubes in MIN 9 did not appear in MIN 10, although both had the same chemical environment. As expected, the environment penetrated the crevice formed by the unexpanded tube and the tube sheet. However, metallographic sections of both the tubes and the tube sheet adjacent to the areas of penetration showed no detrimental effects.

Fig. 29. MIX 10--Appearance After Test

Examination of the tubing after cleaning revealed some attack of the secondary surface. Some incipient attack and a few shallow isolated pits--the deepest was three mils--were found. The attack was slightly more prevalent on the surface that was exposed to vapor than on the surface exposed to liquid. The extent of pitting suggested possible ferrite contamination of the tubing after fabrication was completed, because of the carbon steel shell.

The exceptional resistance of Inconel to corrosive attack under severe environmental exposure is obvious. The Inconel tubing in this test vessel, after more than 3000 hours in a hot solution containing high chloride, some oxygen and numerous other dissolved materials, suffered only minor attack. The tubing suffered very little general corrosion.

d. MIN 11

The secondary environment of MIN 11 contained 1000 ppm Cl and the pH was maintained at 10 with a solution containing 33% Na_3PO_4 and 67% Na_2HPO_4. There was no chemical treatment to remove oxygen but the secondary make-up tank was maintained at 180° F to expel dissolved gases. This maintained the oxygen concentration at somewhat less than 0.5 ppm. Other conditions were the same as those used for MIN 10.

MIN 11 was tested 3024 hours without failure. Figure 30 shows the appearance of the tubes after the test. X-ray diffraction analysis showed that $CaSO_4$ was the major constituent and $CaCO_3$ was the minor constituent of the film that was formed on the tubes in both the vapor and the liquid phases. Although the tubes exposed to vapor were covered with boiler scale, there were some isolated areas which showed bright metal. The tube surfaces were bright and lustrous after cleaning.

The tube with the expanded joints showed no environmental penetration in either phase, but the environment penetrated the unexpanded tube joints. The tests with MIN 10 and MIN 11 were indistinguishable in results with respect to the minor environmental difference of pH adjustment. There was isolated incipient attack with a few shallow pits, up to about 5 mils deep, in MIN 11.

2. Analysis of Results

The performance of the Inconel tubes in all the vessels was very good. It is far superior to any material tested previously. The severe conditions under which all the test vessels were operated had little effect on Inconel.

Fig. 30. MIN 11--Appearance After Test

F. TESTS WITH MONEL VESSELS (MIN 13 AND 14)

The Monel heat exchanger tubes were fabricated from the same heat of material that was used in the Monel autoclave test coupons. The tube sheet body was 1020 carbon steel with nickel overlay on the primary side. The secondary shell was 1030 carbon steel. These vessels had dynamic secondary systems. Deionized water was used for make-up.

1. Tests and Test Results

a. MIN 13

The secondary environment in MIN 13 contained 1000 ppm Cl and the pH was adjusted to 10 with a solution containing 67% disodium phosphate and 33% trisodium phosphate. MIN 13 was tested for 1393 hours. The appearance of the tubes before cleaning is shown in Fig. 31. The secondary surfaces, excluding the tube sheet crevice surfaces, were free of any measurable quantities of foreign matter and showed only a very thin film of gray discoloration on both vapor and liquid surfaces. X-ray diffraction identified Fe_3O_4 as the major constituent in the deposit found on the tubes in both liquid and vapor phases. The film of corrosion products found on the tubes in the liquid phase was slightly darker than the film in the vapor phase. All the tube-to-tube sheet joints were expanded in MIN 13, thus excluding the environment. Pits were found on the secondary surfaces which ranged in depth to about 3 mils. Figure 32 shows a typical area of attack in the vapor and liquid phases.

b. MIN 14

MIN 14 contained secondary water of reactor quality--0.5 ppm Cl maximum, pH 10 with a trisodium phosphate solution free of "excess hydroxide" according to the Whirl-Purcell (Ref. 5) curve, 10 ppm SO_3 and 200 ppm maximum total solids. On occasion, there was some minor carry-over of chloride into MIN 14, which necessitated flushing with demineralized water until the chloride concentration was within specification.

MIN 14 was tested for 1418 hours. The film on the submerged tubes was slightly darker than the tubes exposed to vapor. Figure 33 shows the tubes after the secondary shell was removed. In MIN 14, all tube-to-tube sheet joints were expanded and there was no penetration of any of the joints. The results, so far as pitting was concerned, nearly duplicated the results of MIN 13, with one difference. The extent of pitting and incipient attack was somewhat less. However, the difference in the number of areas attacked did not reflect the

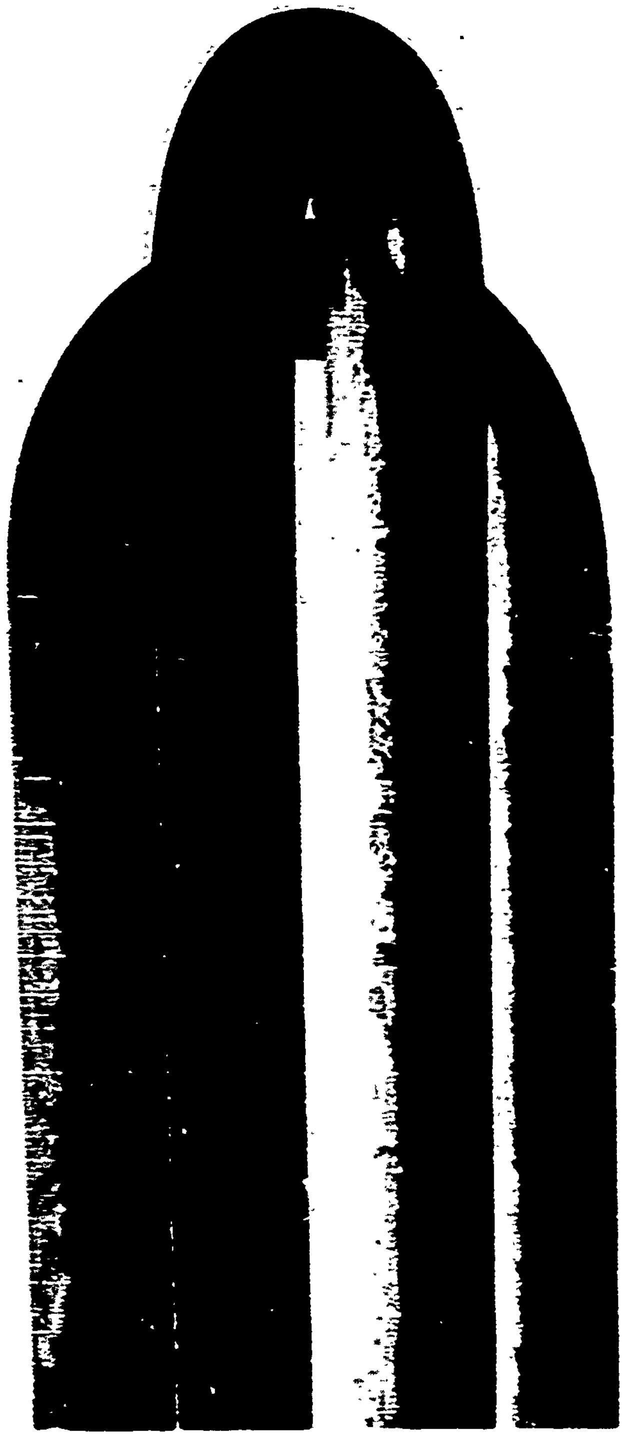
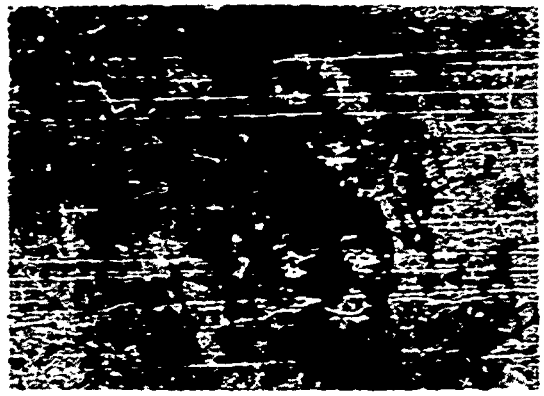


Fig. 31. MIN 13--Appearance After Test



Vapor phase:
Penetration = 1.5 mils

Water phase:
Penetration = 1.1 mils

Fig. 32. MIN 13--Typical Pitted Areas
(30 x Mag)

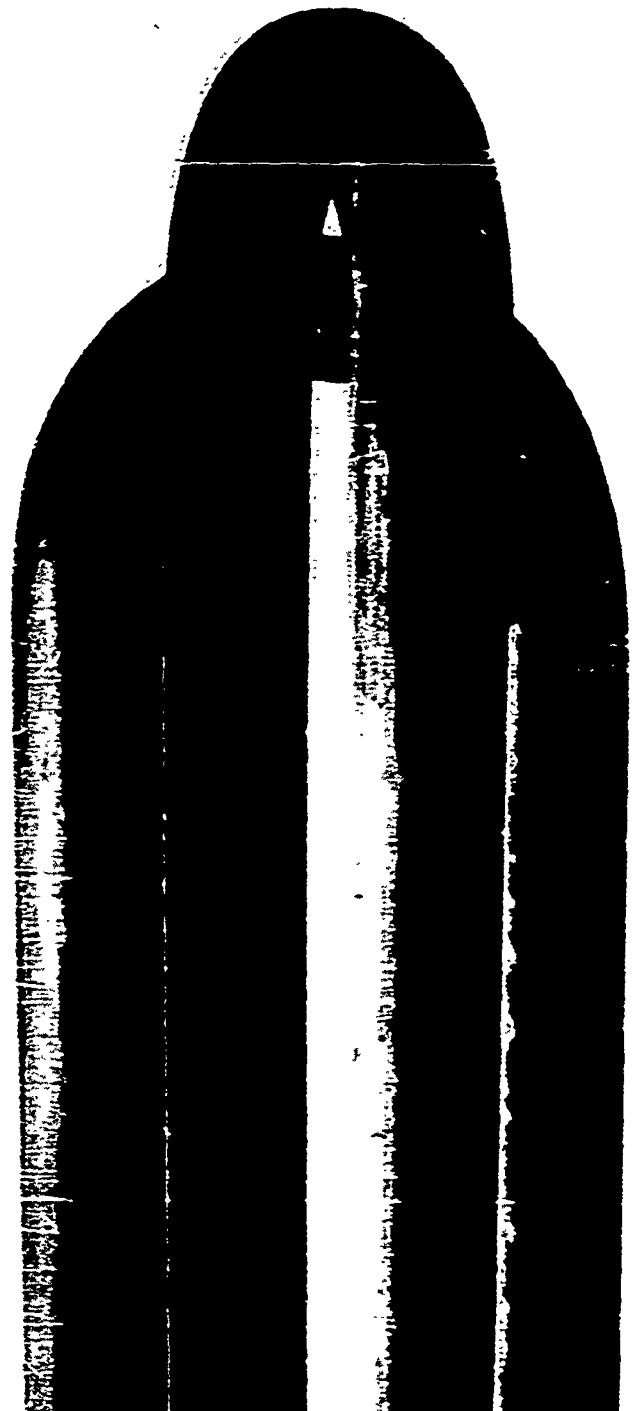


Fig. 33. MIN 14--Appearance After 1418 Hours of Testing

difference in test environment, at least with respect to dissolved chloride. The secondary environment of MIN 13 contained 1060 ppm Cl, while the environment of MIN 14 was virtually chloride free; therefore, pitting may be independent of the presence of chloride.

2. Analysis of Results

Monel showed good resistance to general corrosion. However, the Monel tubing showed considerably more incipient attack and pits than were found on the Inconel tubes. The ratio of pits to areas of incipient attack was greater also than that found on the Inconel.

G. TESTS WITH BIMETAL (MIN 15 AND 16)

The two bimetal heat exchangers were constructed identically. Each had a carbon steel 1030 tube sheet with Type 308 stainless steel overlay and a 1030 carbon steel secondary shell. Type 308 filler metal was used for all welds. The primary side of the hairpin tubes was AISI Type 304 stainless steel, 0.032 inch thick, and the secondary side was 1020 carbon steel 0.032 inch thick. These vessels were tested dynamically along with MIN 10 and 11. Tap water was used for make-up.

The tests with MIN 15 and 16 were intended to define the extent of galvanic protection in the bimetal system. MIN 16 was intentionally defected by filing away the low carbon steel facing the secondary environment to expose the stainless steel. Defects of two sizes, 1/8 inch by 1/8 inch and 1/8 inch by 3/4 inch were machined on the tubing exposed to the vapor phase, the liquid phase and at the vapor liquid interface.

1. Tests and Results

a. MIN 15

The water conditions for MIN 15 were 800 ppm Cl and pH adjusted to 10 with a solution containing 33% Na_3PO_4 and 67% Na_2HPO_4.

MIN 15 was tested for 3019 hours. The tubes were heavily coated with corrosion products and scale, as shown in Fig. 34. X-ray diffraction identified the major constituent on the submerged tubes to be $CaCO_3$ and the minor constituent to be Fe_3O_4 with a trace of $CaSO_4$. The major constituent of the deposit in the vapor phase was found to be Fe_3O_4 with traces of $CaCO_3$ and $CaSO_4$. All the tubes were expanded into the tube sheet. There was no penetration of any of these joints. The tubes were badly pitted, particularly in the vapor phase.

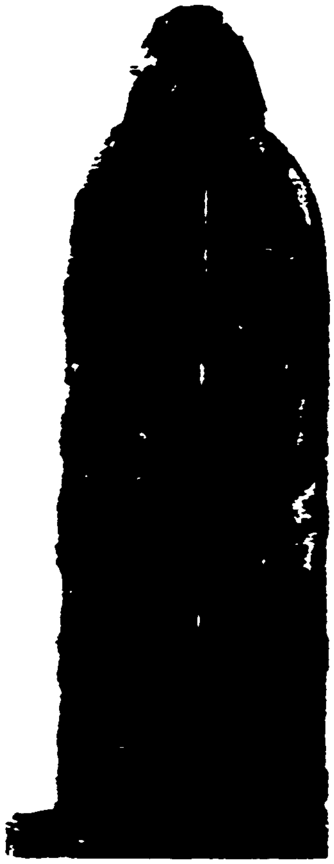


Fig. 34. MIN 15--Appearance After 3019 Hours of Testing

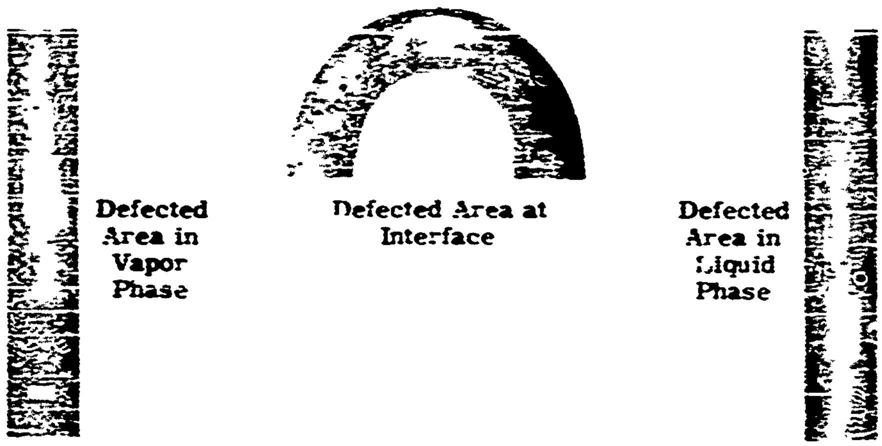


Fig. 35. MIN 16--Appearance After Testing and Descaling

There were a number of areas where the low carbon steel secondary clad had been penetrated completely, exposing small areas of stainless steel. The stainless steel suffered no detrimental effects from exposure to the severe environment, presumably because of cathodic protection by the surrounding sacrificial, low carbon steel anode.

b. MIN 16

The environmental conditions of MIN 16 were identical to those of MIN 15. MIN 16 was tested for 3035 hours. After testing, the tubes appeared similar to those in MIN 15. The composition of the scale was the same, and the portion of the tubes that was exposed to the vapor phase had the same dark, almost black, corrosion products as found in MIN 15. The tubing in MIN 16 was purposely defected by exposing the stainless steel sublayer, as is illustrated in Fig. 35. The defects and the extent of corrosion are clearly visible. Gross amounts of the low carbon steel clad were corroded away. Metallographic sections from the areas of the defects revealed no detrimental effects as far as the stainless steel was concerned.

2. Analysis of Results

The most striking result was the excellent resistance of the submerged low carbon steel tubing to the severe environment.

A rigid definition of the extent of cathodic protection in these tests is very difficult. It could easily be argued that the chance exposure of a crack susceptible area (an area where stresses are adequate for cracking, needing only exposure to water which contains oxygen and chloride at high temperature) is remote; therefore, the fact that cracks did not occur in the specific area exposed does not prove anything conclusively. However, the fact that the AISI Type 304 stainless steel did not crack cannot be completely disregarded. The gross loss of the low carbon steel outer clad from the tubing on the vapor phase is no proof that cathodic protection was in effect. Considering the conditions, i.e., a nearly dry boiler scale, it is doubtful if cathodic protection could operate. It appears that additional tests, designed specifically for the purpose, are required to obtain a final answer.

All the tubes were expanded into the tube sheet. The environment was effectively excluded.

H. TESTS WITH NICKEL VESSELS (MIN 18 AND 19)

These vessels were tested dynamically. Demineralized water was used for make-up.

1. Tests and Results

a. MIN 18

The secondary environment in MIN 18 contained 1000 ppm Cl and the pH was adjusted to 10 with a solution containing 67% disodium phosphate and 33% trisodium phosphate.

MIN 18 was tested for 1385 hours. Figure 36 shows a closeup of the tubes before they were cleaned. The secondary surfaces were free of any measurable quantity of a corrosion film. There was a dark gray discoloration on the tube surfaces in both vapor and liquid phases. The thin deposit on the tubes was mostly Fe_3O_4 in both the vapor and liquid phases. There was a very small deposit of corrosion products at the interface. The submerged portions of the tubes were slightly darker than the portions exposed to the vapor phase. In MIN 18, all the tube-to-tube sheet joints were expanded, and there was no penetration of the joints by the secondary environment. The tubing was pitted and the extent of attack was about equal to the attack on the Monel tubes in MIN 13. There was little difference in the extent of attack between the vapor and liquid phases. The pits ranged up to 3 mils in depth.

b. MIN 19

The environment of MIN 19 contained 0.5 ppm Cl maximum, 10 ppm SO_3, 200 ppm maximum total solids and pH was adjusted to 10 with a trisodium phosphate solution free of "excess hydroxide" according to the Whirl-Purcell curve. It was necessary on occasion to flush the secondary system of MIN 19 to reduce the slight excess of chloride which accumulated.

MIN 19 was tested for 1359 hours. Figure 37 shows a closeup of the tubes before cleaning. Fe_3O_4 was the major constituent of the deposit in both the vapor and liquid phases. The vapor-liquid interface was not as pronounced as the interface in MIN 18. Generally, the overall appearance was about the same as MIN 18. All the tube-to-tube sheet joints were expanded in MIN 19, which excluded the secondary environment. Some incipient attack and pitting occurred in this vessel also. The extent of attack was about the same as that in MIN 18 and was comparable to that in MIN 13 and 14, the Monel test

Fig. 36. MIN 18--Appearance After 1385 Hours of Testing

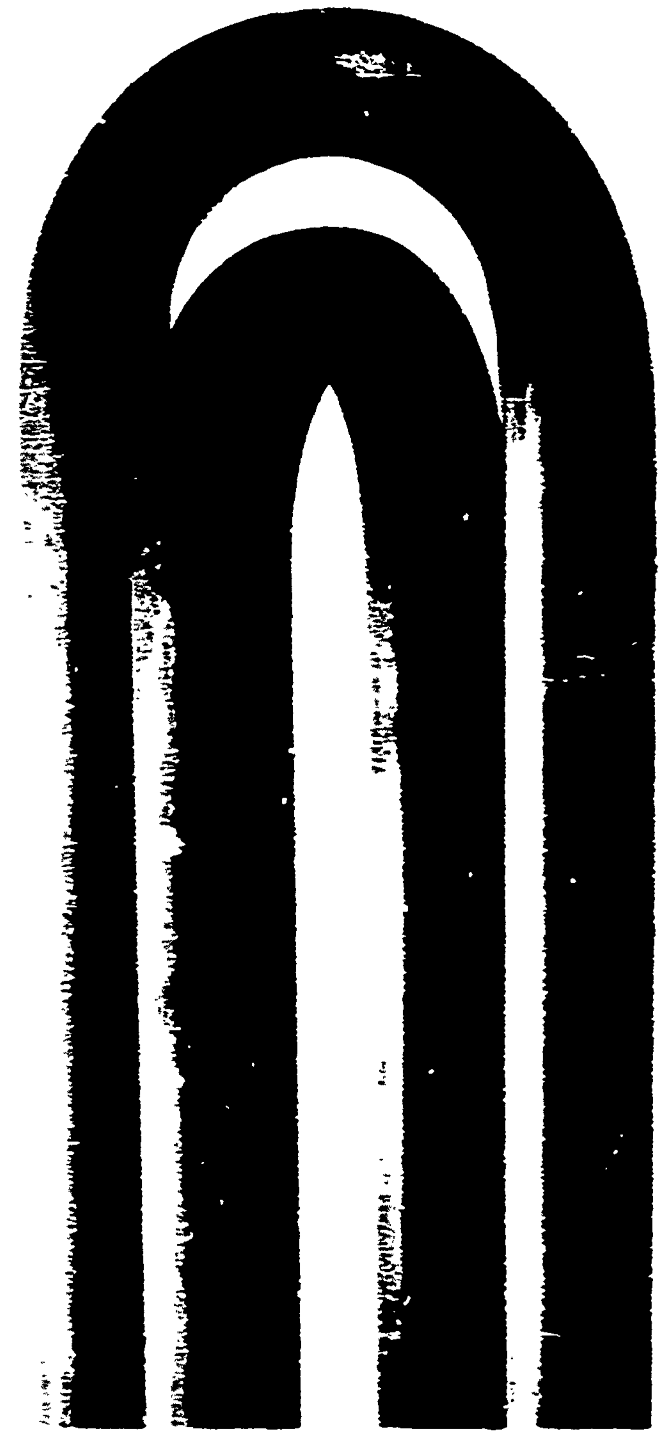


Fig. 37 MIN 19--Appearance After 1350 Hours of Testing

vessels. The fact that both vessels, MIN 18 and MIN 19, were attacked indicates that attack may not be dependent upon the presence of chloride. The extent of attack was about the same in both phases.

2. Analysis of Results

The results with nickel closely approximate the results with Monel.

VI. MODEL HEAT EXCHANGER TESTING

Sets of model heat exchangers (a set consists of a steam generator and superheater) were fabricated, using the following materials: Type 304 stainless steel, Croloy 16-1, Inconel and bimetal (carbon steel secondary-stainless steel primary). Chemical compositions of the materials are summarized in Appendix A.

A. GENERAL DESCRIPTION

1. Design

Model vessels of the design shown in Fig. 38 were used to test materials of construction of both steam generator and superheater configurations. The steam generator and superheater are separate units. The only differences are a blowdown port in the steam generator and a flow baffle in the superheater. The length of the tubes from tube sheet to top of bend is about 25 inches, and the tubes are 1/2- or 3/4-inch OD with an 0.065-inch wall. The tube sheet is 2-3/4 inches thick. Each unit consists of three subassemblies: (1) tubes and tube sheet, (2) secondary shell and (3) primary shell. A summary of the materials used in the construction of the vessels tested is shown in Table 8.

2. Fabrication

Most of the fabrication methods used for the model vessels are quite similar to those employed for miniature vessels. (See Section V-A-2.) The tubes are first assembled into the tube sheet. An expander is used to roll all tubes for a length equivalent to the thickness of the tube sheet plus 0.250 inch. The tubes are weld-sealed on the primary side and the weld overlays made when necessary. No overlay is required on the AISI Type 304 vessels, but overlays are required on the others. After welding the secondary shell to the tube sheet, the assembly is helium leak-tested with a mass spectrometer. Finally, the assembly is completed by welding the primary shell to the tube sheet. The primary side is hydrostatically tested to 3375 psi and the secondary side to 675 psi. None of the vessels received any heat treatment.

3. Environmental Control

Numerous analyses and chemical adjustments were necessary to maintain the specified environments. Control of individual environments was somewhat difficult because of incidental entrainment of dissolved solids, which transported environmental chemicals from the steam

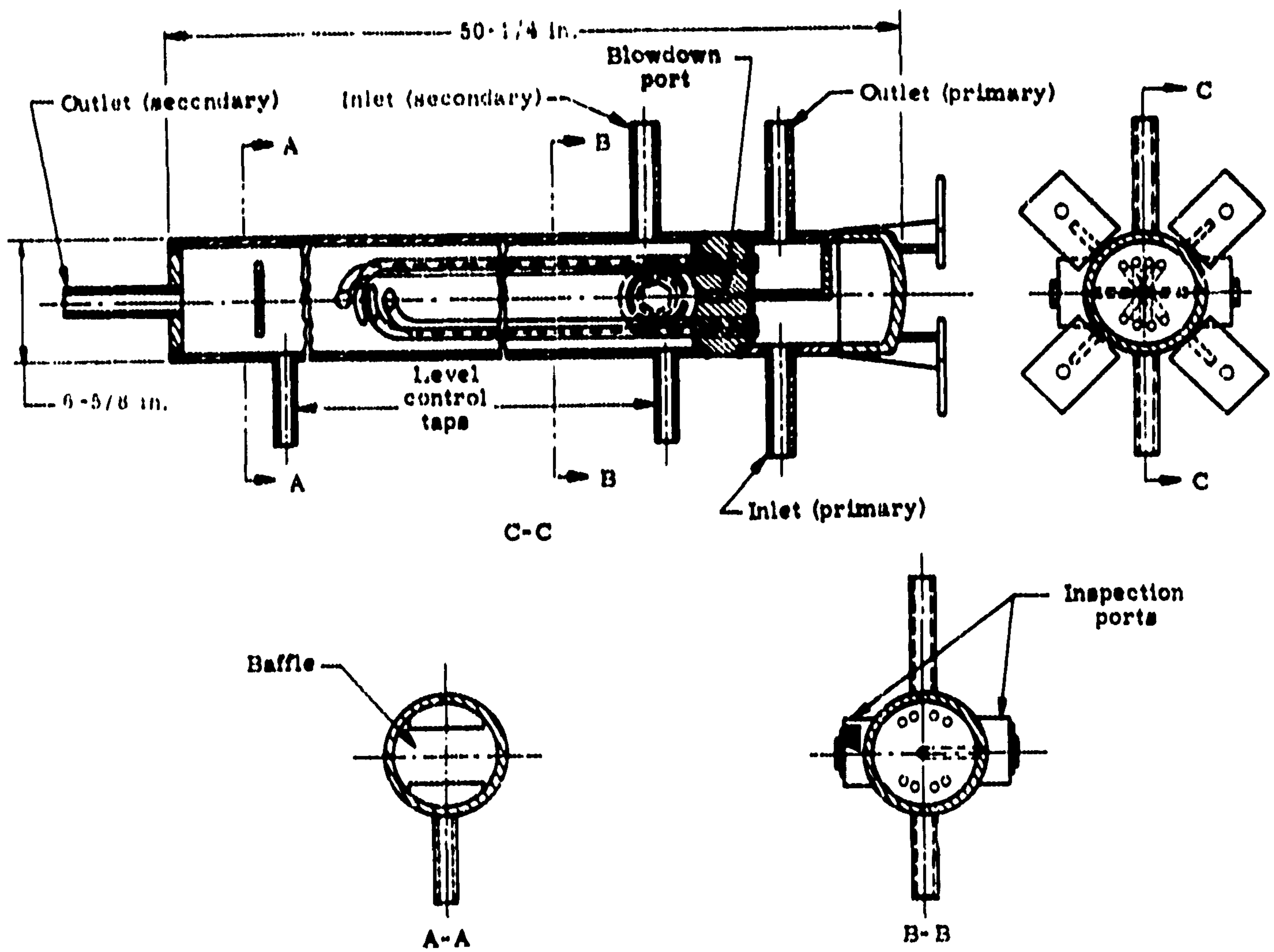


Fig. 38. Model Heat Exchanger Design

generator through the superheater and condensate return to the make-up tank. Corrosion products from the wrought iron pipe in the secondary system in front of the steam generator contributed to the problem of proper environmental control. Model exchangers SX-1, SX-2, SX-5 and SX-6 were tested with one feed pump and one make-up tank serving two sets of vessels, as did the condensate return line. Intermixing of environments occurred frequently. Intermixing of environmental chemicals stopped when the system was divided into two entities with a secondary system for each of the two sets of model heat exchangers.

4. Pretest and Post-Test Evaluation

See Sections V-A-3 and 4 under Miniature Heat Exchangers. The same procedures are pertinent for the model heat exchangers.

B. TESTS WITH TYPE 304 STAINLESS STEEL VESSELS (SG-1 AND SH-1)

1. Tests and Results

The initial water treatment of the secondary water was very similar to one used by commercial water treatment firms: 40 to 50 ppm chloride, 40 to 80 ppm phosphate and sulfite 6 to 10 ppm with pH 10.5 to 10.8. The stainless steel vessels, SX-1, were tested for 1927 hours.

a. Steam generator (SG-1)

The primary surfaces of the 304 stainless steel steam generator were coated with an adherent uniform dark film. Preferential or localized attack were not observed. Metallographic examination of the heat-affected zones in the tube sheet and tube walls disclosed considerable grain boundary carbide precipitation, but no evidence of preferential attack. The secondary surfaces were coated uniformly with a deposited layer of rust-colored corrosion product. X-ray examination indicated that this consisted of alpha-Fe_2O_3 and Fe_3O_4. The layer was relatively adherent, but much of the coating could be removed by brushing. Figure 39 shows the tube assembly as removed from the shell after test. Chemical cleaning of the tubes yielded bright reflective surfaces. Micro examination of the tube and tube sheet disclosed complete freedom from cracking. Sectioning of the tube sheet showed that only limited leakage of water into the crevice area had occurred.

b. Superheater (SH-1)

Testing of the 304 stainless steel superheater was discontinued because of a leak which developed in the wall of the vessel after 1927

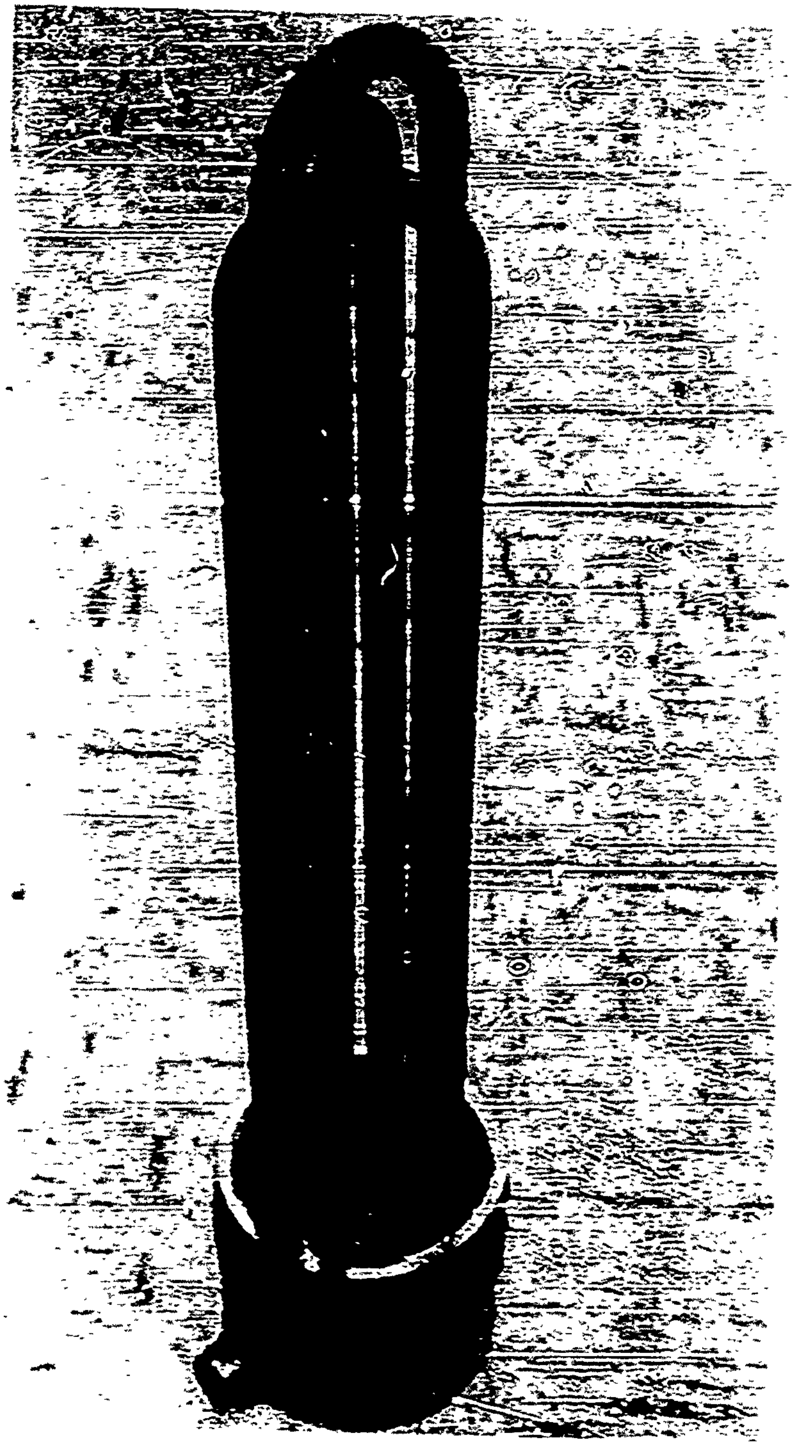


Fig. 39. Type 304SS Steam Generator, SG-1, After Test

hours of test time. Figure 40 is a photograph of the area of failure. Major leakage occurred in the tube sheet section between two circumferential welds, with a small amount issuing from an adjacent leak in the secondary shell. The tube sheet and the attached shell sections were cut longitudinally, as shown in Fig. 41, to expose the cracks which caused the failure of the unit. Micro examination of the labeled sections in the figure showed that cracking started in the tube sheet at the end of the secondary shell crevice and propagated inward, mainly in an angular direction toward the centermost portions of the tube sheet. Cracks also propagated to the periphery of the tube sheet, which resulted in the main leak. Closer visual examination of the edge of the tube sheet exposed several other cracks of 1/4 inch and greater which, however, did not show signs of leakage. At the point of leakage in the tube sheet, the crack propagated through the secondary shell weld and into the shell itself, where additional leakage occurred. The failure exhibited typical transgranular stress corrosion cracking. Higher magnification photographs of the large crack as shown in Fig. 42 give evidence of considerable grain boundary attack along side branches of the main crack due to sensitization from the heat of welding. Extensive cracking of the secondary surface of the tube sheet could be seen by the unaided eye.

Sections made through the tube holes which were checked with a dye penetrant test revealed the extent of cracking which occurred in the tube sheet. This is shown in Fig. 43. The portions of the tube holes shown in Fig. 43 are approximately 2-3/4 inches long. Penetration of liquid and corrosion products along the tube crevice from the secondary chamber varied from 1 to 1-1/2 inches, relatively consistent with the lengths of cracks along the holes on the tube sheet.

Extensive cracking of the tube wall was also found in the areas of leakage. Figure 44 shows cracks in a tube wall, as revealed by dye penetrant. The cracks extended completely through the tubes in many cases, making it possible to snap the half-sections of tubing in two by hand. Dye penetrant checks and metallographic examination of the tube sections above the tube sheet revealed no evidence of cracking.

The primary surfaces showed the typical dark, adherent coating and no evidence of cracking. The secondary surfaces of the tubes and tube sheet were covered with a very thin reddish-brown adherent film similar in appearance to that on the secondary surfaces of the steam generator.

2. Analysis of Results

There is no doubt that Type 304 stainless steel and probably all of the austenitic stainless steels are not applicable in heat exchangers unless both the primary and secondary water systems are demineralized

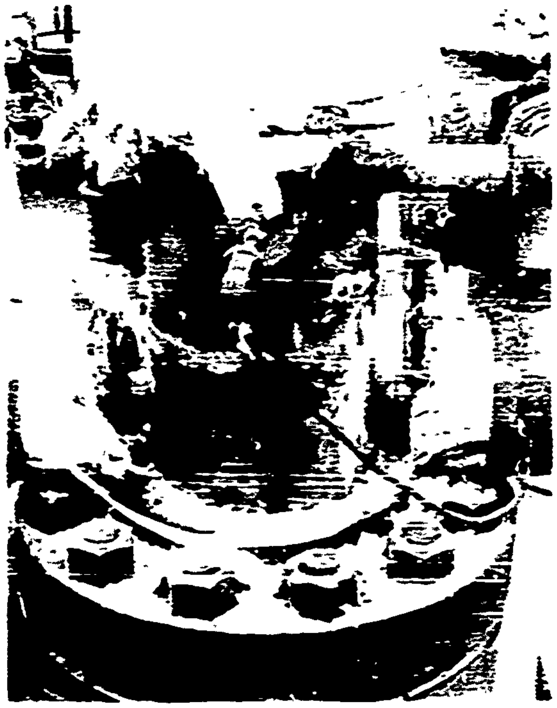


Fig. 40. Point of Leakage in Type 304 Stainless Steel Steam Superheater--MOD SH-1

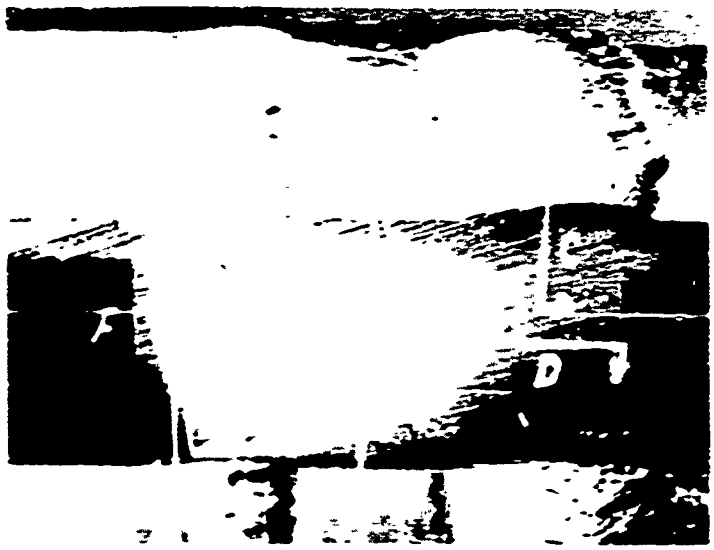


Fig. 41. Sectional Steam Superheater at Location of Failure--MOD SH-1

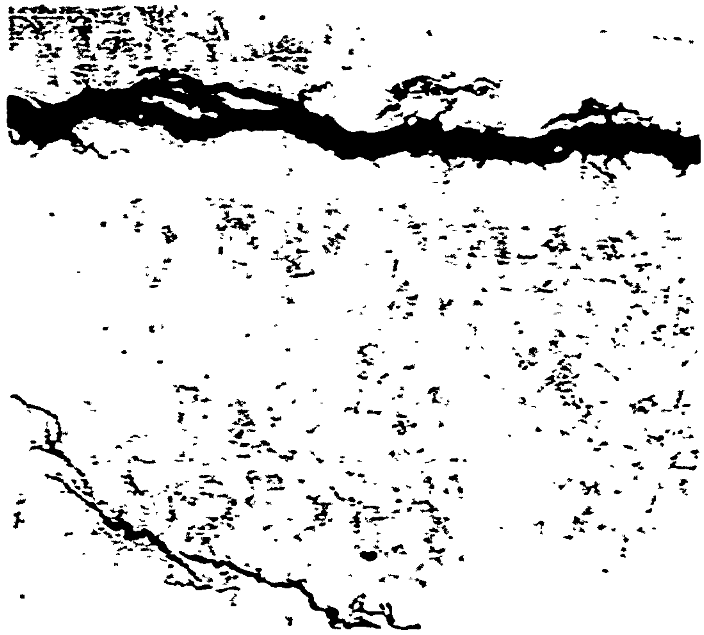


Fig. 42a. Stress Corrosion Cracks in Superheater Shell SH-1
100x Magn

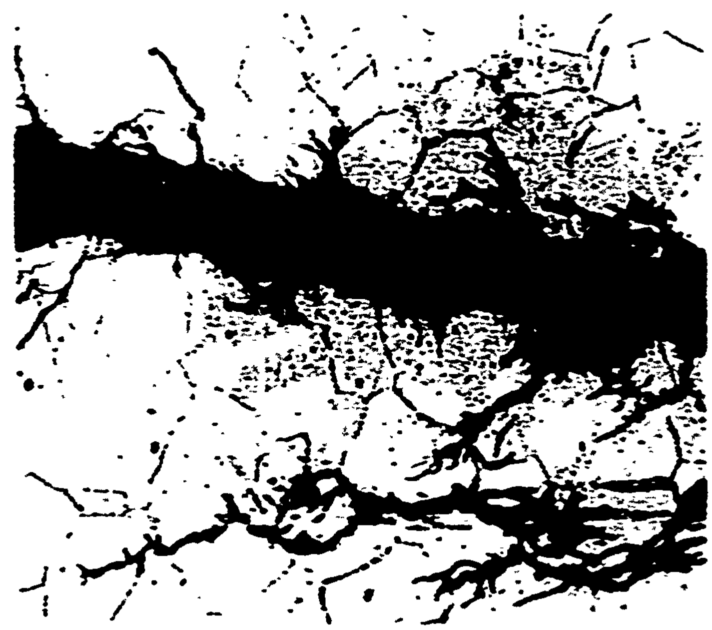


Fig. 42b. Grain Boundary Attack Along Main Stress Corrosion Crack 500x Magn

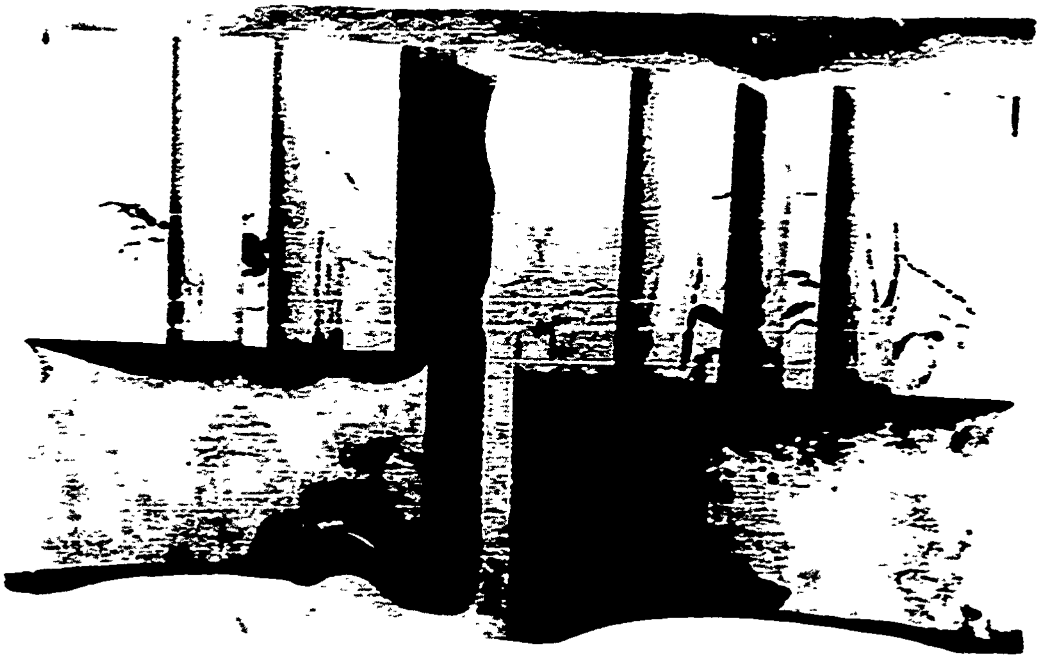


Fig. 43. Cracking in Superheater Tube Sheet Sections as Indicated by Dye Penetrant--MOD SH-1

Fig. 44. Cracks in Expanded Portion of Superheater Tube as Indicated by Dye Penetrant--MOD SH-1

and particular care taken to eliminate all oxygen. The early failure of the 304 stainless steel superheater confirmed that stressed austenitic steels are readily susceptible to stress corrosion cracking. The entrainment of oxygen, while actually very low in percentage, together with intermittent foaming or other phenomena which permitted dissolved boiler constituents to enter the superheater and become concentrated as evaporation progresses, created conditions conducive to cracking in the superheater.

C. TESTS WITH BIMETAL VESSELS (SG-2, SH-2, SG-4 AND SH-4)

The bimetal model heat exchangers were constructed analogous to the bimetal miniature heat exchanger. Only carbon steel contacted the secondary environment.

1. Tests and Results

The original environment in SG-2 was 40 to 50 ppm Cl, 40 to 80 ppm PO_4, 6 to 10 ppm SO_3 with pH 10.5 to 10.8. This treatment was modified after 3853 hours of test to include only a control of chloride, pH and oxygen, with the chloride concentration increased to 800 to 1000 ppm.

The water conditions used to test the bimetal steam generator, SG-4, were those specified for the SM-1 reactor. The desired environmental controls were: 0.5 ppm chloride, maximum < 0.5 ppm oxygen controlled by maintaining 10 ppm sodium sulfite, 200 ppm total solids maximum, and pH adjusted to 8.5 with trisodium phosphate. Some difficulty was encountered with chloride contamination. The source of the chloride contamination was finally traced to a thin film of corrosion products, from a previous test, in the blowdown coil. The occluded chloride was leached slowly from the corrosion film into the secondary solution. The blowdown coil had been cleaned after previous use, but apparently a thin film remained. After recleaning the coil and after an extended flushing of the secondary system with demineralized water, the chloride concentration remained within specification. During the entire testing period, the secondary make-up tank was maintained at 180° F to expel most of the oxygen.

a. Steam generator (SG-2)

This steam generator was service tested 5041 hours, along with the bimetal superheater. The primary surfaces of the heat exchanger were entirely free of foreign deposits, but contained a uniform and adherent dark film. The secondary surfaces of the tubes, tube sheet and shell wall underwent extensive general corrosion and were covered

by a loosely adhering film of corrosion products. X-ray analysis of the deposit showed it to consist of alpha-Fe_2O_3 and Fe_3O_4. There was extensive pitting of the surfaces, particularly under the tubercular growths. Figure 45 shows the surface tuberculations as emphasized by oblique lighting. Areas of small and large pits are readily apparent.

The large pits numbered about 50 per tube and often penetrated to the stainless steel. Figure 46 shows sections of the tubes at some of the large pits. In some cases, several square millimeters of stainless steel surface were exposed. Only slight attack occurred in the high carbon zone of the stainless steel clad interface. There was no evidence of pitting or stress corrosion cracking in the stainless steel at these points.

The tube-to-tube sheet crevices remained sealed from the secondary water for the greater portion of their lengths. The water generally penetrated the crevice approximately 1/4 to 1 inch from the secondary tube sheet surface. Little corrosion occurred at these points.

The ID surface (stainless steel) of the tube contained a high degree of grain boundary carbide precipitation in the heat-affected zone near the weld. The high carbon zone was approximately 0.002 inch in depth and can be attributed to pickup during normal tube fabrication. The unheated portions of the tube were completely free of precipitated carbides at the surface. In no case, however, was there evidence of preferential grain boundary attack from the high purity primary water after 22 months of contact.

b. Superheater (SH-2)

The secondary surfaces of the tubes in contact with the steam were extensively corroded. The zones outside the flow-baffle area suffered general deep pitting; in particular, the area adjacent to the tube sheet was deeply pitted. The area under the baffle was generally pitted and had isolated areas of general corrosion, about 1/2 inch in diameter, which penetrated to approximately 70 to 90% of the carbon steel wall thickness. The attack was similar to that shown in Fig. 46. The smaller pits, covering the entire tube surfaces, were about 0.040 to 0.080 inch in diameter by about 0.020 inch deep and about 100 per square inch. Figure 47 shows examples of the pitting corrosion and the large heavily corroded areas found under the flow baffle. The tube-to-tube sheet crevices remained sealed from the secondary, as did those in the steam generator. A heavy deposit of loose, scaly corrosion product was found on the secondary tube sheet surface. X-ray examination of the surface deposits showed that they were composed of alpha-Fe_2O_3 and Fe_3O_4.

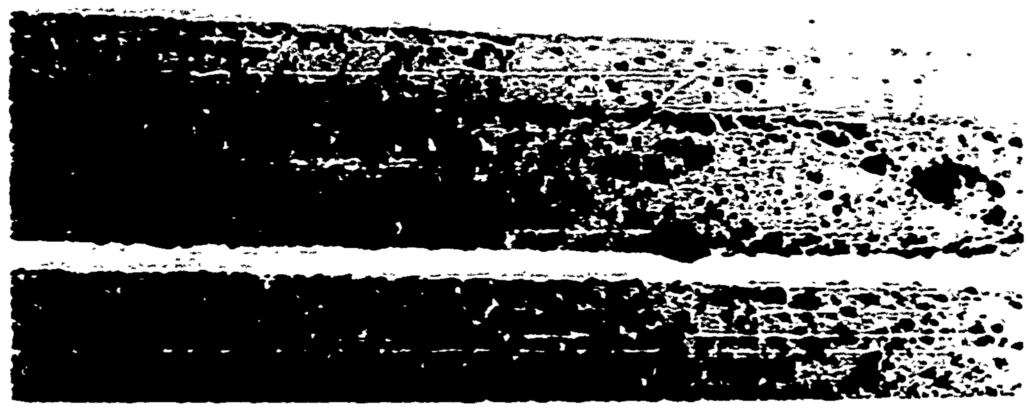


Fig. 45. Surface Blistering Observed Under Oblique Lighting--MOD SG-2

Fig. 46. Section Through Tubercules in Bimetal Tubing--MOD SG-2

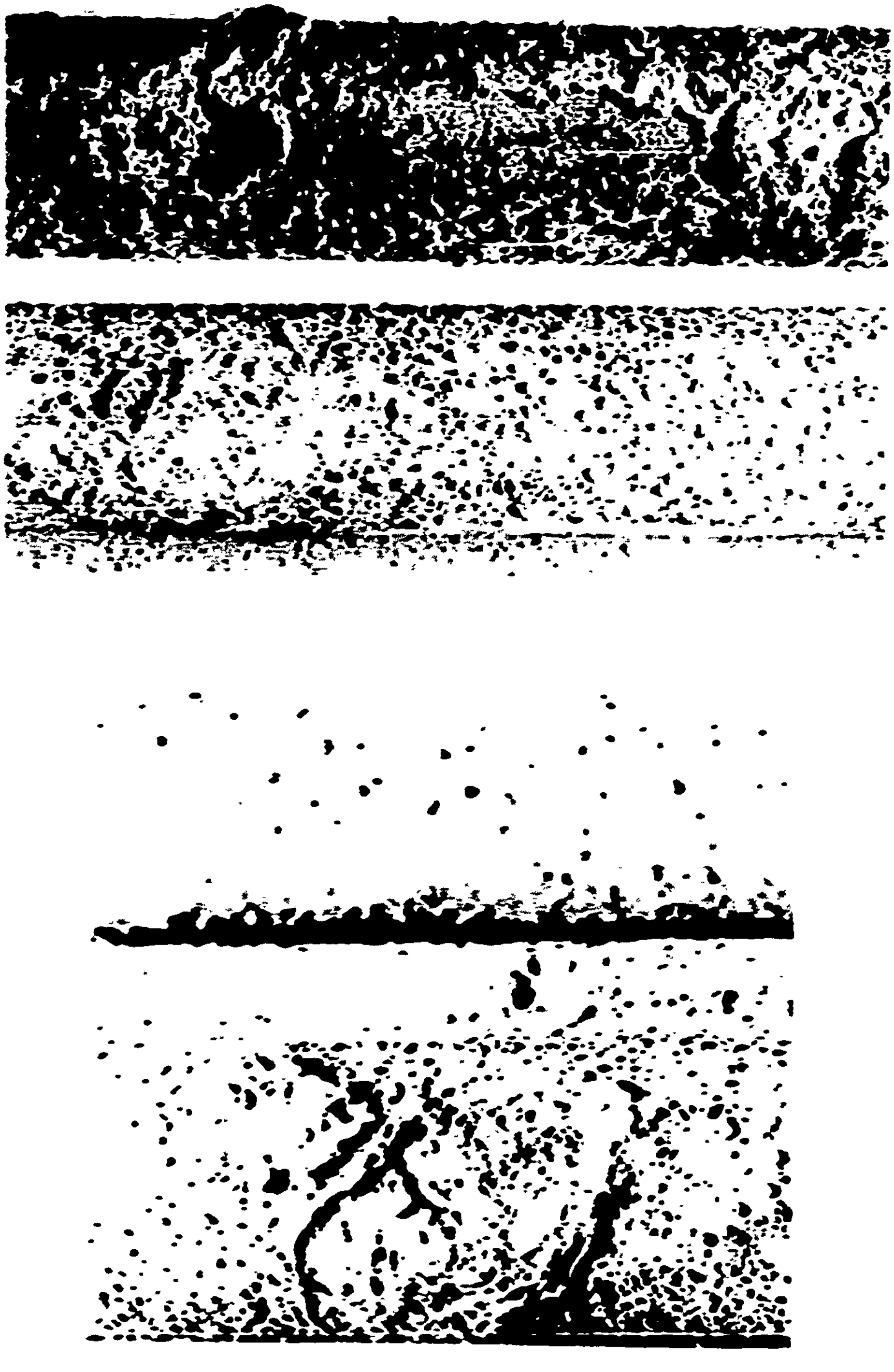


Fig. 47. Surface Corrosion on Bimetal Superheater Tubes--MOD SH-2

c. Steam generator (SG-4)

This bimetal steam generator was service tested for 4890 hours. Figure 48 shows the tubes and tube sheet with the secondary shell removed. The overall appearance of the vessel contrasted sharply with the bimetal steam generator, SG-2. A very small amount of corrosion products was found. The secondary surfaces were covered completely with a reddish-brown deposit. X-ray diffraction of the material scraped from the tubes showed that the principal constituent was Fe_3O_4. Emission spectroscopy showed that iron was almost the exclusive metallic constituent of the deposit. The corrosion products at the base of the tubes on the tube sheet were found to be mixed iron oxides of about the same composition as the deposits on the tubes.

There were no full penetrations of the low carbon steel clad, as occurred in the bimetal steam generator tested previously. The deepest penetration found was 9 mils. The extent of corrosion in SG-4 was clearly much less than that which occurred in SG-2. The test times for the two are comparable. The extent of corrosion in SG-4 was somewhat more than expected, considering that the concentrations of chloride and oxygen were very low.

The tubes of this vessel were expanded into the tube sheet. There was no penetration of the crevice by the secondary environment.

d. Superheater (SH-4)

The superheater was, of course, service tested for 4890 hours, along with the bimetal steam generator. The appearance of the steam generator after the removal of the shell is shown in Fig. 49. The tubes were covered with an adherent reddish-brown deposit. X-ray diffraction analysis showed two principal patterns, Fe_2O_3 and Fe_3O_4, in the corrosion products. Emission spectroscopy showed the principal component to be iron. There was a slightly greater quantity of corrosion products on the tube sheet of the superheater than on the steam generator. X-ray diffraction analysis showed that the corrosion product on the tube sheet had the same composition as the deposit on the tubes. Just as the steam generator from this set was not nearly as corroded as the steam generator from the previously tested set, so the superheater was not nearly as corroded as the one tested earlier. The deepest pit found in the surface of the secondary tubing was about 3.5 mils. The worst pitting was on the tubes near the tube sheet.

2. Analysis of Results

In the dynamic system reported here, where all oxygen was not eliminated, the thick layer of corrosion products reduced the steaming

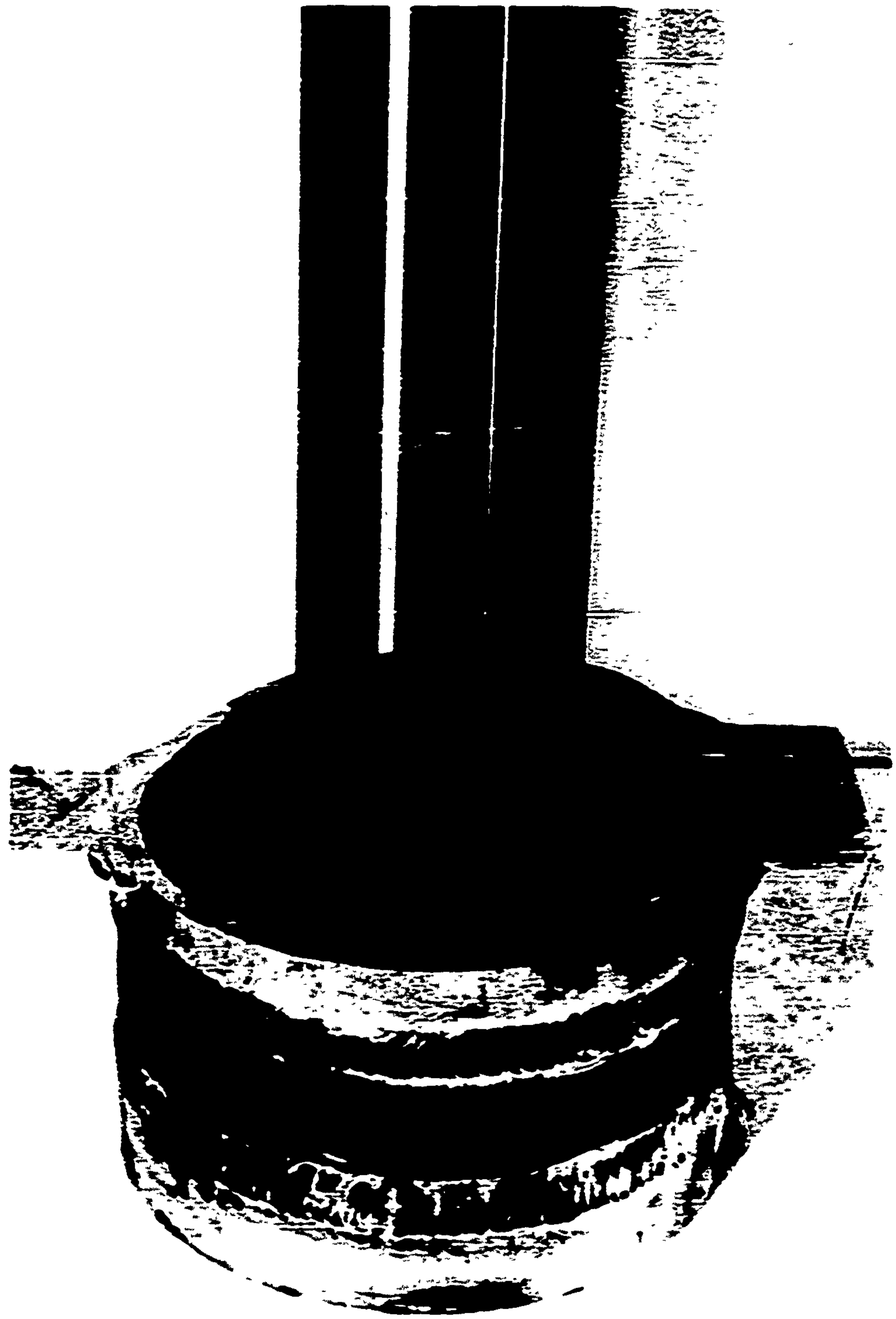


Fig. 46. SG-4- Appearance After 4890 Hours of Testing

Fig. 49. SH-4--Appearance After 4890 Hours of Testing

rate from about 70 lb/hr initially to about 48 lb/hr finally. Considerable difficulty was encountered in maintaining the proper steaming rate and attendant superheat control. Corrosion in the steam generator (SG-4) with no oxygen or chloride was more than expected but the extent of corrosion was clearly much less than in the steam generator (SG-2) containing oxygen. The absence of stress corrosion cracks in the bimetal vessels, as expected, is an indication that low carbon steels, even when stressed, do not experience this phenomenon.

D. TESTS WITH CROLOY 16-1 VESSELS

1. Tests and Results

The desired environmental controls for these test vessels were: 800 to 1000 ppm chloride, pH 8.3 to 9.5 and no oxygen (controlled with sulfite). Considerable difficulty was encountered in trying to maintain these secondary water conditions. Much of this difficulty was traceable to the large amounts of corrosion products which originated mostly in the wrought iron piping in front of the steam generator. The corrosion products were pumped into the steam generator with the make-up water. As the corrosion products settled onto the tube sheet, chloride was occluded onto the particle surfaces. The chloride concentration fluctuated as the deposit on the tube sheet was agitated by action in the steam generator. The use of sulfite was not specified for the control of oxygen, but was arbitrarily adopted in an effort to control its concentration.

a. Steam generator (SG-5)

The Croloy 16-1 steam generator was service tested for 4253 hours. Upon removal of the secondary shell, the appearance of the tubes was as shown in Fig. 50, a closeup of the tube ends. The discontinuous film of corrosion products indicated that active cells, probably pits, occurred beneath. Subsequent investigation showed that this was the case. The depth of pits ranged to two mils. A considerable agglomeration of corrosion products was found at the base of the tubes on the tube sheet.

The interior of the secondary was completely covered with typical red rust to a thickness of about 17 mils. X-ray diffraction of the material scraped from the tubes showed that the principal constituent was Fe_3O_4. X-ray diffraction of the agglomerate from the base of the tubes showed it was composed mainly of $CaCO_3$. Emission spectroscopy identified Ca as the principal component of the agglomerate. It is notable that the two samples of corrosion products were dissimilar, because this fact helped to identify the source. The source of the

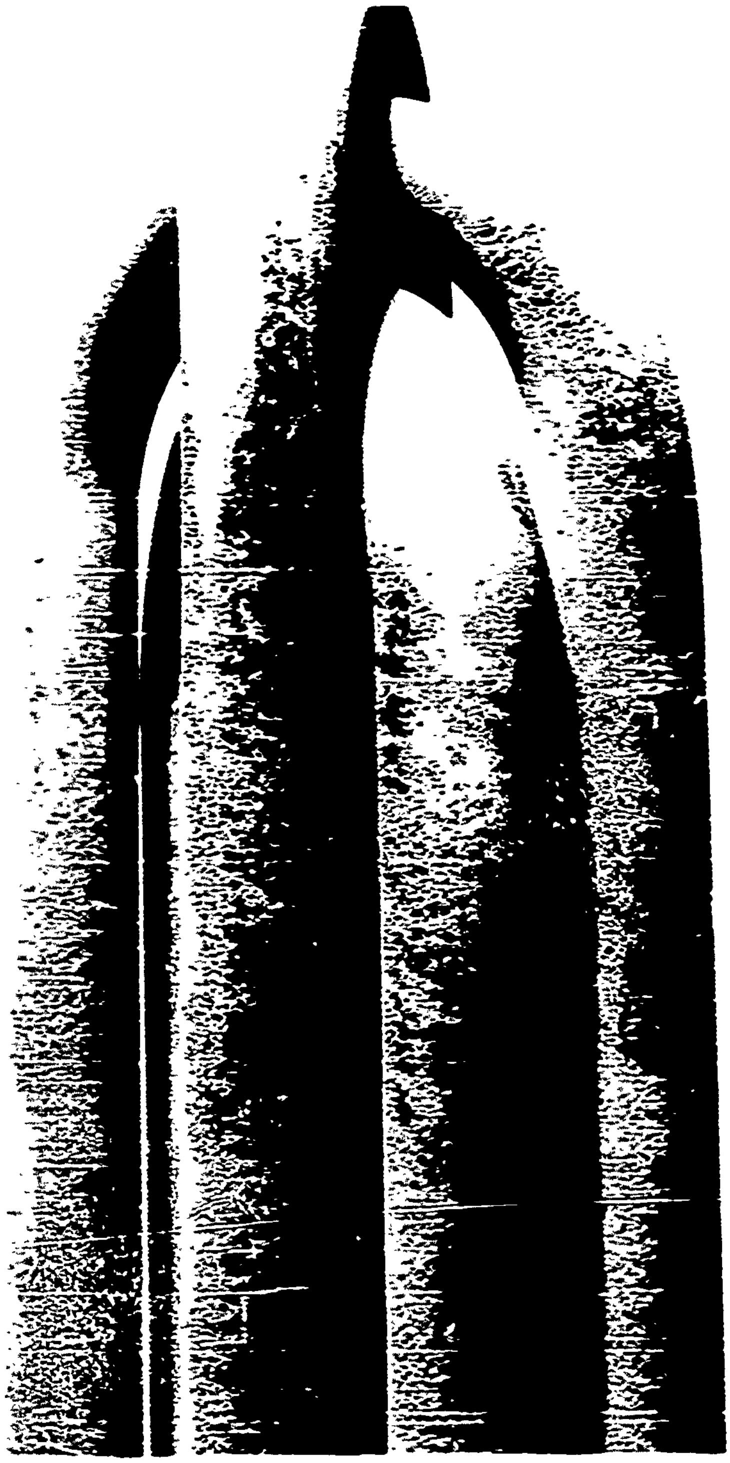


Fig. 50. Close-up of Tubes After Test--SG-5

profuse amount of agglomerated material and loose corrosion products was undoubtedly the secondary feed system. The entire secondary feed system was rebuilt with stainless steel after this test.

All the tubes were rolled into the tube sheet of MOD SG-5. Therefore, environmental chemicals were excluded, except for the first 1/2 inch from the tube sheet surface. No cracks were found in the crevice in the vicinity of the seal weld, as in the Croloy 16-1 miniatures.

b. Superheater (SH-5)

The appearance of the SH-5 superheater after the test is shown in Fig. 51, a closeup of the tubes. Many tuberculations of varying sizes occurred on the tubes. X-ray diffraction of the deposit showed two dominant patterns, NaCl and Fe_3O_4. Emission spectroscopy showed the principal components of the deposit to be Fe and Na.

The depth of pits under the tuberculations ranged to about 40 mils. The tubes, after cleaning, were generally bright metal with many isolated areas containing deep pits. As expected, there was no penetration of the rolled tube crevices by the secondary environment.

2. Analysis of Results

The general resistance of Croloy 16-1 to corrosion was good but, unfortunately, the corrosion which did occur, occurred as pitting. The superheater, SH-5, was pitted severely, which prevents an estimation of its service life. Extensive pitting to half the thickness of the tube wall was found in many areas.

E. TESTS WITH INCONEL VESSELS (SG-6, SH-6, SG-7 AND SH-7)

1. Tests and Results

The environment in the SG-6 steam generator was 800 to 1000 ppm chloride with pH 8.3 to 9.5 and no oxygen (controlled with sulfite). In contrast, the secondary environment in SG-7 steam generator was 9.5 ppm chloride, 150 ppm phosphate, 10 ppm sulfite, with total solids 175 to 200 ppm and pH 10 to 10.5.

In SG-7 and SH-7, 1/2-inch Inconel tubing was substituted for the usual 3/4-inch tubing normally used in the test heat exchangers. The design was modified slightly to provide equivalent heat transfer surface.

Fig. 51. Close-up of Tubes After Test--SH-5

a. Steam generator (SG-6)

This vessel was service tested for 3819 hours. At first glance, the appearance of the tubes in this steam generator was discouraging (see Fig. 52). However, investigation showed that the Inconel was remarkably resistant, even under the severe test conditions. The boiler scale was about 25 mils thick and had just started to flake off. Despite the poor appearance, the only deleterious effect of the boiler scale was a lowering of heat transfer rate. In the areas where flaking occurred, the lustrous surface of the tubes is visible (Fig. 52). After chemically cleaning the tubes, they were bright and lustrous and the surface retained score marks and scratches from fabrication. A few limited areas of surface dulling with smaller areas of incipient surface roughening did occur.

X-ray diffraction of the boiler scale identified the major constituent as $CaSO_4$. The results strongly suggest that in consideration of heat transfer and service, the secondary water should undergo some purification before it enters the steam generator.

The environmental chemicals did not penetrate the tube-to-tube sheet crevice. The tubes were rolled into the tube sheet. No cracks or pits were found.

b. Superheater (SH-6)

After the 3819-hour test, the tubes of the Inconel superheater appeared as shown in Fig. 53. A gray-white film about four mils thick covered the tubes. X-ray diffraction identified the scale as $CaSO_4$. After cleaning, the tubes appeared similar to those in the steam generator (SG-6), except there was no surface roughening. There was no penetration of the crevice at the rolled tubes in this superheater. No cracks or pits were found.

c. Steam generator (SG-7)

This vessel was service tested for 4747 hours with no failure. Fig. 54 shows the tubes after test. The tubes were covered with a thin, adherent reddish-brown deposit which X-ray diffraction analysis identified as mixed iron oxides, mostly Fe_2O_3. After cleaning, the tubes appeared bright and lustrous, as shown in Fig. 55.

The agglomerate of corrosion products on the tube sheet at the base of the tubes had the same composition as the coating on the tubes, except for a minor inclusion of $CaCO_3$. No corrosion products were

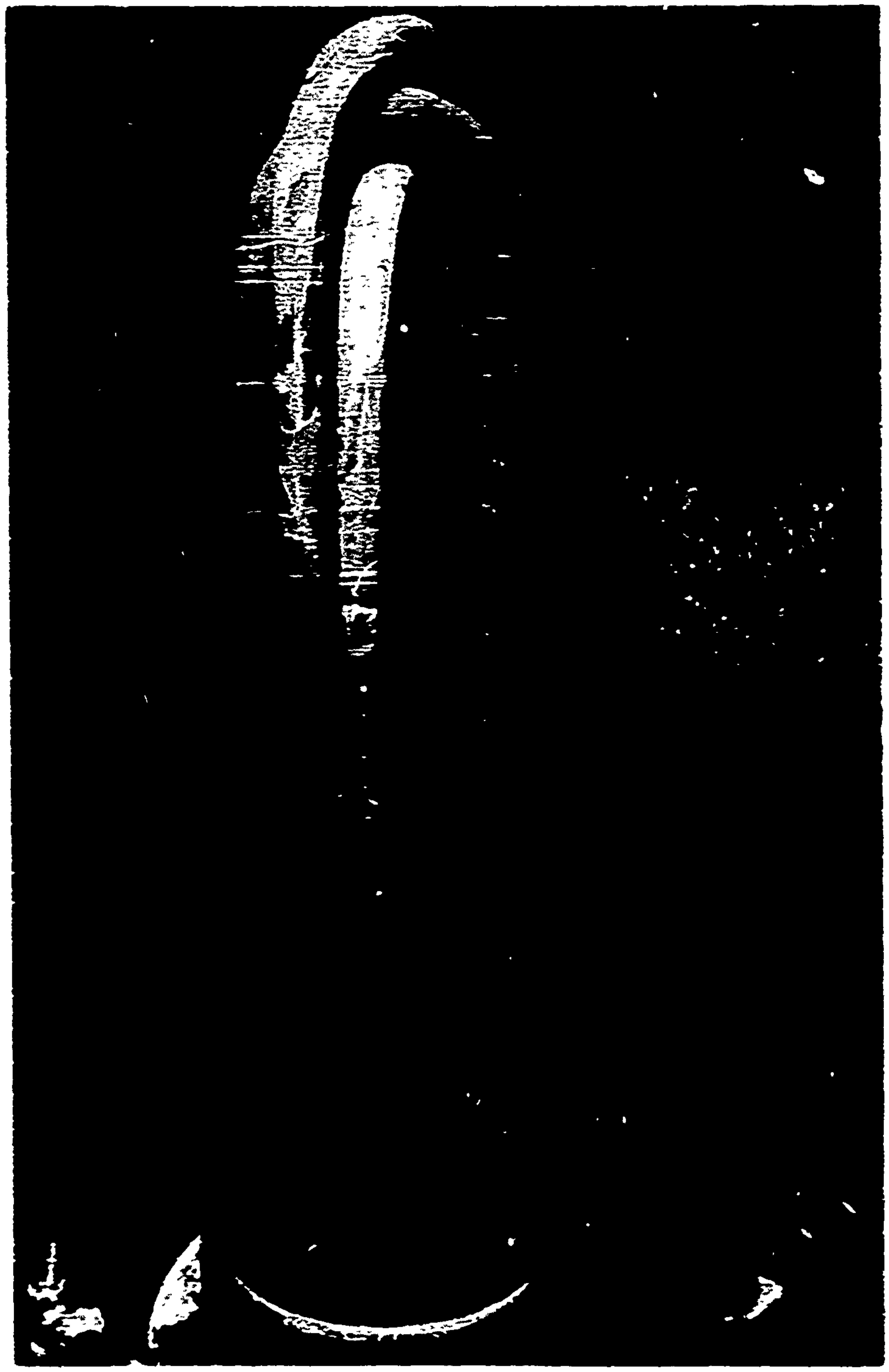


Fig. 52. View of Tubes with Secondary Shell Removed--SG-6

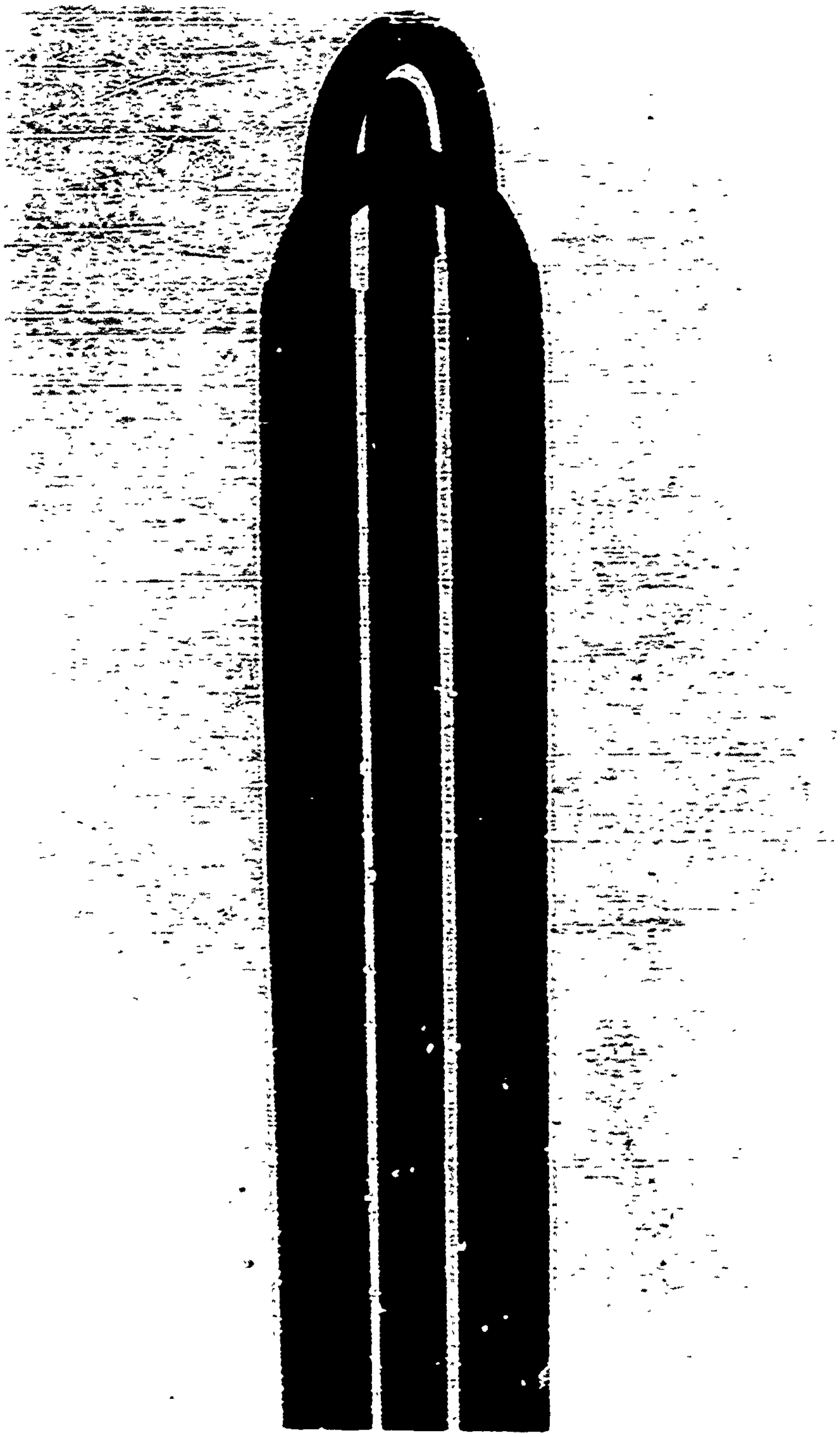


Fig. 53. Overall View of Tubes with Secondary Shell Removed--MOD SH-5

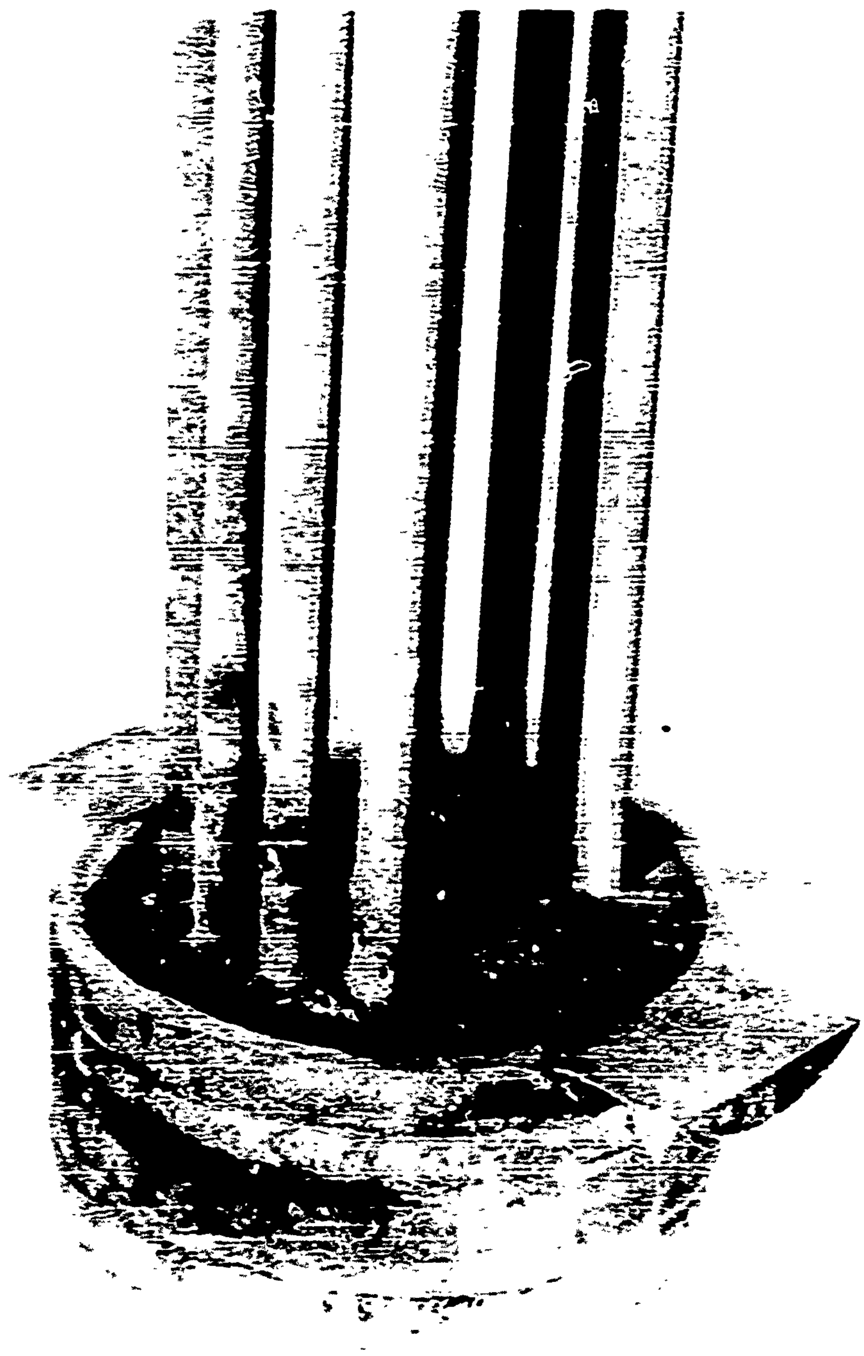


Fig. 54   Appearance After 1747 Hours of Testing--SG-7

Fig. 55. Appearance After Cleaning--SX-7

found in the crevice between the expanded tube and the tube sheet. No cracks or pits were found on any of the secondary surfaces of the Inconel tubing.

d. Superheater (SH-7)

The superheater was tested 4747 hours, along with the steam generator. The tubes appeared as shown in Fig. 56 after removal of the secondary shell. The tubes were covered with a loosely attached, pale, reddish-brown film very similar to the film on the tubes in the Inconel steam generator SG-7. The principal constituents were identified as Fe_3O_4 and Fe_2O_3 by X-ray diffraction analysis. Emission spectroscopy showed that the metallic constituent was almost exclusively Fe. After cleaning, the tubes were similar in appearance to those from the steam generator (see Fig. 55). No cracks or pits were found in any of the Inconel tubing. There was no environmental penetration of the crevice between the expanded tube and the tube sheet.

2. Analysis of Results

Inconel was the best material tested. The Inconel tubes in the steam generator and the superheater which were tested in reactor quality water were almost completely unaffected by the environment. Even when exposed to water which contained a high concentration of dissolved chloride, Inconel showed a resistance superior to all other materials tested.

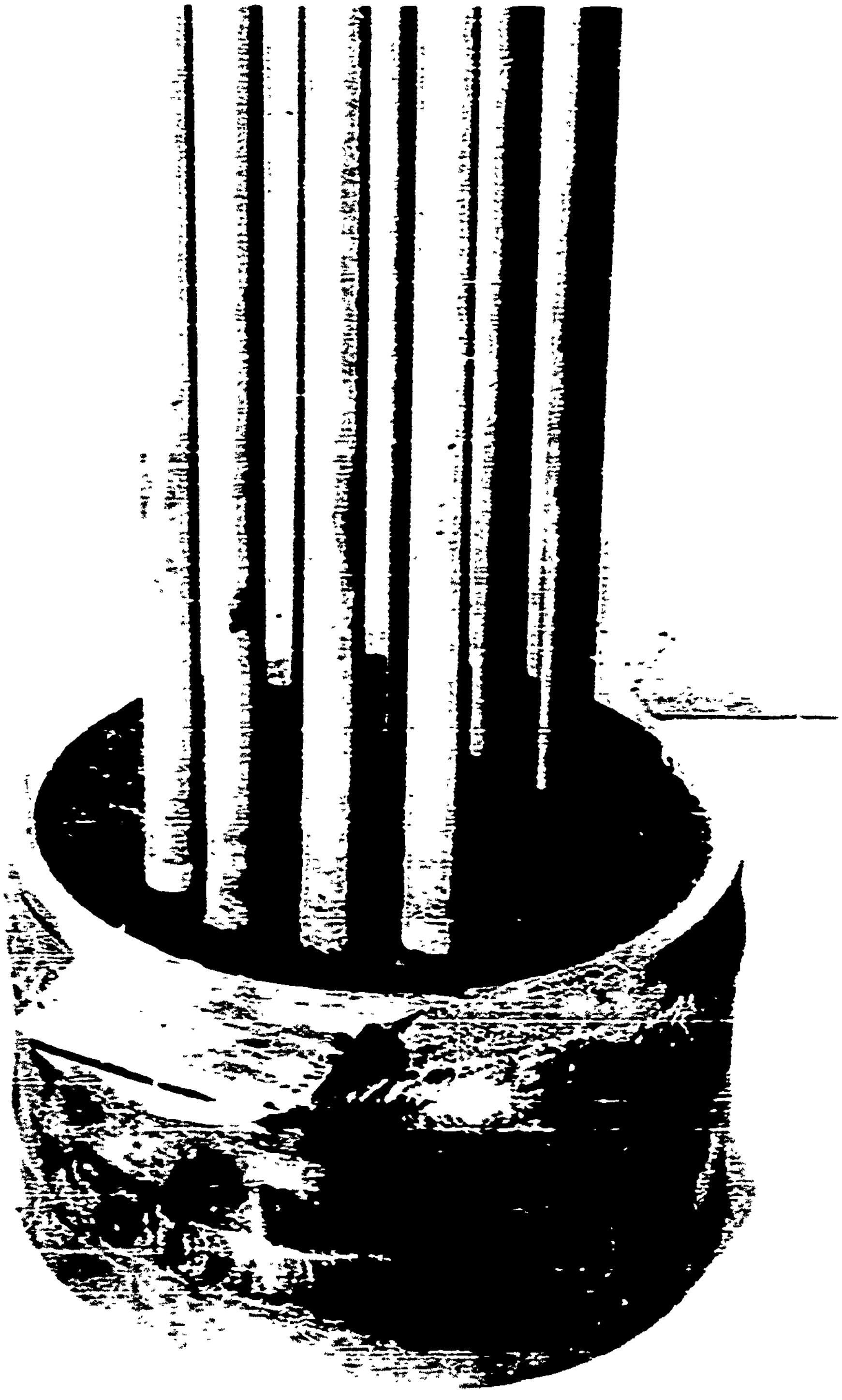


Fig. 56. Appearance After 4747 Hours of Testing--SH-7

VII. CONCLUSIONS

Of the metals tested, only the austenitic stainless steel, AISI Type 304, suffered stress corrosion cracking. The ferritic stainless steel, Croloy 16-1 and low-carbon steel pitted extensively. Monel and nickel were pitted slightly. Inconel was attacked only superficially.

Admittedly, the test environments in most cases were severe; but this was intentional and was specified to emphasize differences between the various metals tested. On the basis of these several tests, Type 304 stainless steel and Croloy 16-1 must be rejected for long term use in heat exchangers, unless elaborate precautions are taken to remove detrimental constituents from the secondary environment and also from the primary environment. The applicability of low-carbon steel is in doubt even with a high purity secondary environment.

Monel and nickel pitted slightly in a pure, as well as an impure, secondary environment. The severity of the attack did not appear to be related to the chloride concentrations in the respective environments. The attack, albeit very slight, particularly in the high purity environment, must result in ranking these materials below Inconel in the evaluation for steam generator service.

By all criteria, Inconel was far superior to any material tested. Even in a very severe environment with extended exposure at high temperature, Inconel suffered hardly more than superficial attack. On the basis of the several tests reported here, we must conclude that Inconel is the most serviceable material yet tested for steam generator and superheater service.

Rolling of the heat exchanger tubes into the tube sheet should continue to be specified. In these tests, there was very limited, if any, penetration of crevices formed by the tubes which had been expanded into the tube sheet, whereas there was always penetration in the crevices where tubes were not expanded. In the vapor phase, the penetration always continued to the seal-weld of the tube-to-tube sheet. Concentration of solids in the crevice and potential detrimental effects due to corrosion can be eliminated rather cheaply by rolling. In addition, tube fit-up is improved and the probability of weld defects greatly reduced.

Little can be added to the state of the art concerning the treatment of secondary water for use in a steam generator fabricated with Inconel tubes and low-carbon steel shell and tube sheet. In our tests, the concentration of chloride and/or oxygen appeared to be unrelated to the incipient attack which Inconel suffered. Needless to say, sufficient treatment to remove boiler scale anions, calcium and magnesium, is required. Evaporators are applicable for this purpose. The incidental

removal of chloride along with the calcium and magnesium is beneficial because of its definite adverse affect on the low-carbon steel components of the heat exchanger. Deaerators effectively remove dissolved gases from the evaporator feedwater. Injection of sulfite or other oxygen scavengers into the secondary feedwater removes the last traces of oxygen.

By all appearances, Inconel is sufficiently resistant to highly impure environments to withstand untreated secondary water. However, the problem of boiler scale formation would be virtually insurmountable. The carbon steel tube sheet and shell would most likely be the portions of the steam generator which would suffer most in untreated secondary water.

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APPENDIX A

Chemical Composition of Autoclave Coupons and Heat Exchanger Tube Materials

Material	Ni	Cr	Fe	Mn	Si	Cu	C	Ti	P	S	Mo
	Composition (%)										
304 SS autoclave coupons	9.67	17.57	rem	1.55	0.43		0.076		0.025	0.022	0.26
410 SS autoclave coupons	0.17	15.47	rem	0.40	0.25		0.068				2.45
Inconel autoclave coupons	76.6	15.85	7.20	0.20	0.20	0.10	0.040			0.007	
Monel autoclave coupons	65.0		1.00			33.00					
Nickel "A" autoclave coupons	99.50		0.07	0.28	0.04	0.02	0.09				
MIN 1, 2 and 3 tubes (304 SS)	9.67	17.57		1.55	0.43		0.076		0.025	0.022	0.26
MIN 4, 5 and 6 Croloy 16-1 tubes	1.88	15.25	rem	0.56	0.25		0.04				
MIN 7, 15 and 16 bimetal tubes											
Outer clad 1020 CS*			rem	0.45			0.20		0.04 max	0.05 max	
Inner wall 304 SS	9.67	17.57		1.55	0.43		0.076		0.025	0.022	0.26
MIN 8, 9, 10 and 11 Inconel tubes	75.4	15.3	8.7	0.23	0.20	0.07	0.04	2.6			
MIN 12, 13 and 14 Monel tubes	65.0		1.11	0.95	0.16	32.65	0.12				
MIN 17, 18 and 19 nickel "A" tubes	99.5		0.07	0.28	0.04	0.02	0.09				
SX-1 and SX-3 304 SS tubes	9.67	17.57	rem	1.55	0.43		0.076		0.025	0.022	0.26
SX-2 and SX-4 bimetal tubes											
Outer clad 1020 SS*			rem	0.45			0.20		0.04 max	0.05 max	
Inner wall 304 SS	9.67	17.57	rem	1.55	0.43		0.076		0.025	0.022	0.26
SX-5 Croloy 16-1 tubes	1.89	15.25	rem	0.56	0.25		0.04				
SX-6 and SX-7 Inconel tubes	75.6	15.6	7.12	0.15	0.16	0.04	0.03				

*Nominal composition

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C. Eicheldinger
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The results of these tests have shown conclusively that Inconel is superior to all other materials tested in simulated nuclear service. A wide range of environments from high purity water to water containing high chloride concentrations was used. The criteria of comparison were: resistance to general corrosion, pitting corrosion, crevice corrosion and susceptibility to stress corrosion cracking.

AISI Type 304 austenitic stainless steel, AISI Type 430 ferritic stainless steel, Inconel, Monel and nickel were tested in tilting autoclaves. Test exposures varied considerably, as did environmental composition. The Type 304 stainless steel cracked severely in 120-hour tests. The Type 430 stainless steel pitted badly in 120-hour tests. Inconel suffered very slight incipient attack after 2000 hours' exposure to a severe environment. Both Monel and nickel pitted somewhat after 2000 hours' exposure to a severe environment.

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Miniature heat exchangers tubed with AISI Type 304 stainless steel, Croloy 16-1, bimetal with low-carbon steel facing the secondary, Inconel, Monel and nickel were tested for varying times in a wide range of environments. Two of the three Type 304 stainless steel heat exchangers cracked and failed within a short time, one after only 43 hours' exposure. Two of the three Croloy 16-1 vessels failed, and all three suffered rather severe pitting. None of the three bimetal miniature vessels with low carbon steel on the secondary side failed, but all showed varying degrees of pitting and gross loss of surface metal. The four Inconel vessels suffered nothing more than superficial attack, even after long exposures to environments containing high concentrations of dissolved chloride. The two Monel vessels and the two nickel vessels were pitted to varying degrees.

Model configuration heat exchangers tubed with AISI Type 304 stainless steel, Croloy 16-1, bimetal with low carbon steel facing the secondary, and Inconel were tested under conditions comparable to the miniature vessels. The model vessels were tested in sets consisting of one steam generator and one superheater in series. The superheater of the Type 304 stainless steel set failed after about 3000 hours. The secondary environment on the steam generator contained about 50 ppm chloride. The two sets of bimetal model heat exchangers suffered varying degrees of corrosion in proportion to their conditions of exposure. The set with Croloy 16-1 tubes, particularly the superheater, pitted severely. The Inconel test vessels (two sets) were attacked only superficially. No Monel or nickel model heat exchangers were tested in this phase of the program.

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Model configuration heat exchangers tubed with AISI Type 304 stainless steel, Croloy 16-1, bimetal with low carbon steel facing the secondary, and Inconel were tested under conditions comparable to the miniature vessels. The model vessels were tested in sets consisting of one steam generator and one superheater in series. The superheater of the Type 304 stainless steel set failed after about 3000 hours. The secondary environment on the steam generator contained about 50 ppm chloride. The two sets of bimetal model heat exchangers suffered varying degrees of corrosion in proportion to their conditions of exposure. The set with Croloy 16-1 tubes, particularly the superheater, pitted severely. The Inconel test vessels (two sets) were attacked only superficially. No Monel or nickel model heat exchangers were tested in this phase of the program.

MARTIN

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